Electronic Supplementary Information

Title: (±)-Applanatumines B–D: novel dimeric meroterpenoids from *Ganoderma applanatum* as inhibitors of JAK3

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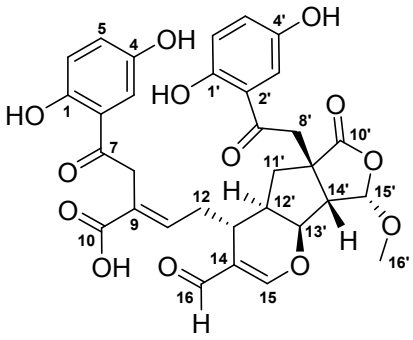
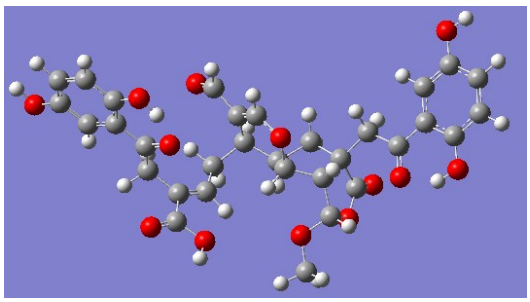
Contents

1. ECD calculations of 1–3.

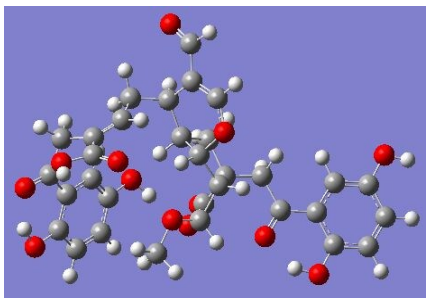
ECD calculation methods. The CONFLEX 7 searches based on molecular mechanics with MMFF94S force fields were performed for model compounds of **1**–**3**, respectively. The predominant conformers were optimized and calculated by DFT calculation at B3LYP/6-311G(d,p) level with the PCM in MeOH. Under the circumstances, all the above calculations were carried out with the Gaussian 09 package of programs. For comparison of the calculated curves and experimental CD spectra, the program SpecDis was used.



Applanatumin B (**1**)



1a



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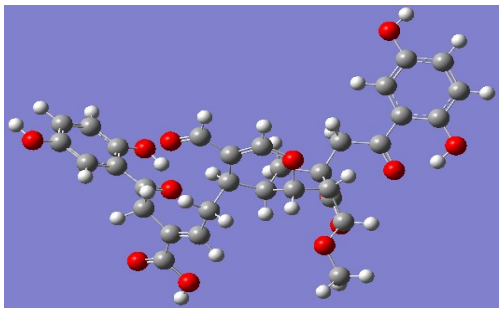

1c

Figure S1. Optimized geometries of predominant conformers for compound **1** at the

B3LYP/6-31G(d,p) level in MeOH.

Table S1. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **1** at B3LYP/6-311G (d,p) level in MeOH.

conformer	E+ZPE	G	%
1a	–2215.422555	–2215.502019	7.5
1b	–2215.417959	–2215.494029	0.0
1c	–2215.424173	–2215.504390	92.5

E+ZPE, G: total energy with zero point energy (ZPE) and Gibbs free energy at 298.15 K, %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors

Standard orientation of 1a at B3LYP/6-311G (d,p) level in MeOH:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	8.171742	-1.797389	-1.544480
2	6	0	8.085715	-3.063013	-0.990314
3	6	0	7.019586	-3.400089	-0.141820
4	6	0	6.049899	-2.452639	0.136970
5	6	0	6.115096	-1.156957	-0.416173
6	6	0	7.199223	-0.828136	-1.271426
7	6	0	5.089571	-0.145523	-0.123640
8	6	0	3.928708	-0.489230	0.791353
9	8	0	5.157887	0.991911	-0.609329
10	6	0	2.895457	0.630796	0.971611
11	8	0	6.891313	-4.636279	0.430549
12	8	0	7.341276	0.385058	-1.840997
13	6	0	3.557727	1.897782	1.513973
14	8	0	4.251480	1.982485	2.494264
15	8	0	3.233205	2.975730	0.773062
16	6	0	-7.254696	-2.924230	-1.379200
17	6	0	-8.243075	-2.667237	-0.443885
18	6	0	-8.126846	-1.579878	0.434815
19	6	0	-7.011610	-0.762391	0.359015
20	6	0	-5.992506	-1.003196	-0.584385
21	6	0	-6.121936	-2.106739	-1.467428
22	8	0	-5.193923	-2.409907	-2.397573
23	8	0	-9.075921	-1.283511	1.375978

24	6	0	-4.798481	-0.143406	-0.671019
25	6	0	-3.444979	1.887437	0.014970
26	6	0	-2.025397	1.208830	2.030021
27	6	0	-0.826050	0.214355	1.933619
28	6	0	-1.135309	-1.010393	1.108258
29	6	0	-0.484448	-1.280157	-0.046944
30	6	0	-2.084977	-2.004064	1.573654
31	8	0	0.452978	-0.528227	-0.622028
32	8	0	-2.712769	-1.936739	2.622025
33	6	0	0.674940	0.813355	-0.083636
34	6	0	2.487669	2.618150	-0.428139
35	6	0	0.484181	0.855890	1.438351
36	6	0	1.769894	0.184336	1.955517
37	6	0	2.159384	1.110472	-0.312593
38	8	0	1.341130	3.384237	-0.505563
39	6	0	1.565746	4.766469	-0.814230
40	6	0	-2.337773	1.956526	0.771340
41	8	0	-3.913305	-0.368938	-1.502368
42	1	0	-2.219821	-2.873513	0.898718
43	1	0	2.496036	0.604035	-1.215021
44	1	0	0.497642	1.912627	1.722602
45	6	0	-4.650415	1.029091	0.293505
46	6	0	-3.576543	2.741917	-1.195952
47	8	0	-4.595351	2.832000	-1.849603
48	8	0	-2.458891	3.428274	-1.521653
49	1	0	8.993627	-1.534130	-2.198796
50	1	0	8.850456	-3.799927	-1.213967
51	1	0	5.238098	-2.732873	0.794502
52	1	0	3.425467	-1.383199	0.412290
53	1	0	4.334172	-0.759420	1.772318
54	1	0	7.623905	-5.199917	0.156952
55	1	0	6.580252	0.929809	-1.537056
56	1	0	-7.340606	-3.762818	-2.059289
57	1	0	-9.113814	-3.312854	-0.391461
58	1	0	-6.943699	0.069781	1.046649
59	1	0	-4.483881	-1.731543	-2.310372
60	1	0	-9.795088	-1.923379	1.324983
61	1	0	-1.763477	1.946420	2.798426
62	1	0	-2.883959	0.650331	2.400854
63	1	0	-0.666193	-0.125230	2.962599
64	1	0	-0.663071	-2.192534	-0.607048
65	1	0	0.015200	1.477724	-0.635121
66	1	0	3.161697	2.830422	-1.261307
67	1	0	2.001560	0.453129	2.987024

68	1	0	1.667781	-0.903587	1.918050
69	1	0	0.583366	5.214470	-0.949133
70	1	0	2.090859	5.267845	0.001951
71	1	0	2.144186	4.863077	-1.738867
72	1	0	-1.576662	2.658794	0.448018
73	1	0	-4.621589	0.628271	1.308540
74	1	0	-5.554776	1.639825	0.226359
75	1	0	-2.667525	3.955189	-2.307755

Standard orientation of 1b at B3LYP/6-311G (d,p) level in MeOH:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.719312	-1.406579	-0.955868
2	6	0	-8.342231	-0.374619	-0.275391
3	6	0	-7.586649	0.566755	0.441205
4	6	0	-6.207294	0.455608	0.459906
5	6	0	-5.549341	-0.586366	-0.226412
6	6	0	-6.325156	-1.533729	-0.944735
7	6	0	-4.085736	-0.712511	-0.208642
8	6	0	-3.249251	0.293136	0.559625
9	8	0	-3.516666	-1.636902	-0.805397
10	6	0	-1.729046	0.116947	0.430835
11	8	0	-8.155251	1.602683	1.130572
12	8	0	-5.781496	-2.562245	-1.624783
13	6	0	-1.286319	-1.282335	0.864355
14	8	0	-1.470300	-1.790314	1.948298
15	8	0	-0.569285	-1.893101	-0.085099
16	6	0	3.336560	-3.906837	1.057278
17	6	0	2.272779	-3.398584	1.785071
18	6	0	2.214643	-2.031836	2.095155
19	6	0	3.218607	-1.194292	1.642663
20	6	0	4.306010	-1.680280	0.893677
21	6	0	4.373096	-3.072274	0.620237
22	8	0	5.393950	-3.632833	-0.057571
23	8	0	1.212643	-1.480880	2.851482
24	6	0	5.362012	-0.789115	0.381406
25	6	0	4.274183	1.346189	-0.586832
26	6	0	2.653998	2.556467	0.994791
27	6	0	1.102950	2.686047	1.028625
28	6	0	0.588521	3.871061	0.247401
29	6	0	-0.244846	3.731625	-0.809754

30	6	0	0.877179	5.228020	0.677203
31	8	0	-0.673663	2.585521	-1.333738
32	8	0	1.553954	5.525298	1.651895
33	6	0	-0.033958	1.349815	-0.884385
34	6	0	-0.567476	-1.135658	-1.344247
35	6	0	0.354560	1.404644	0.600668
36	6	0	-0.987831	1.166261	1.310442
37	6	0	-1.114820	0.263238	-0.994441
38	8	0	0.710806	-1.080575	-1.844995
39	6	0	1.194744	-2.311716	-2.401724
40	6	0	3.216445	2.132789	-0.322730
41	8	0	6.388903	-1.261521	-0.114984
42	1	0	0.426900	6.022632	0.048176
43	1	0	-1.841361	0.560486	-1.748842
44	1	0	1.000429	0.540278	0.780078
45	6	0	5.212594	0.736657	0.444795
46	6	0	4.598618	1.190973	-2.039398
47	8	0	3.837383	1.419868	-2.956615
48	8	0	5.863939	0.780018	-2.247447
49	1	0	-8.299598	-2.135178	-1.508425
50	1	0	-9.424334	-0.294752	-0.296187
51	1	0	-5.645375	1.191032	1.019553
52	1	0	-3.515486	1.304432	0.240142
53	1	0	-3.524518	0.226933	1.618093
54	1	0	-9.114505	1.565572	1.042894
55	1	0	-4.807569	-2.498974	-1.501998
56	1	0	3.394511	-4.963512	0.826219
57	1	0	1.486444	-4.062251	2.127724
58	1	0	3.152878	-0.147240	1.895438
59	1	0	6.041275	-2.908807	-0.227555
60	1	0	0.382629	-1.969535	2.733547
61	1	0	2.964676	1.891911	1.802977
62	1	0	3.057666	3.543481	1.248072
63	1	0	0.862941	2.876253	2.080159
64	1	0	-0.674552	4.588899	-1.318551
65	1	0	0.806606	1.177332	-1.551772
66	1	0	-1.238316	-1.685578	-2.006942
67	1	0	-0.867361	0.820683	2.337621
68	1	0	-1.572421	2.090133	1.337710
69	1	0	2.148181	-2.080101	-2.871835
70	1	0	1.341738	-3.060007	-1.619943
71	1	0	0.496038	-2.692211	-3.153589
72	1	0	2.724887	2.551546	-1.196548
73	1	0	6.217680	1.131433	0.286019

74	1	0	4.900257	1.033660	1.446024
75	1	0	5.990933	0.704327	-3.205868

Standard orientation of 1c at B3LYP/6-311G (d,p) level in MeOH:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	8.096724	2.031638	-0.483098
2	6	0	7.731597	3.350400	-0.273342
3	6	0	6.382273	3.700155	-0.108953
4	6	0	5.415198	2.711138	-0.157323
5	6	0	5.762308	1.360616	-0.368452
6	6	0	7.130246	1.020214	-0.535257
7	6	0	4.740606	0.305304	-0.421977
8	6	0	3.275975	0.661787	-0.246394
9	8	0	5.054322	-0.877614	-0.613322
10	6	0	2.314323	-0.533987	-0.260733
11	8	0	5.971688	4.988571	0.099753
12	8	0	7.550749	-0.243129	-0.743908
13	6	0	2.450083	-1.323750	-1.562762
14	8	0	2.384556	-0.882508	-2.680965
15	8	0	2.613975	-2.639694	-1.322380
16	6	0	-6.028810	3.583635	-1.580290
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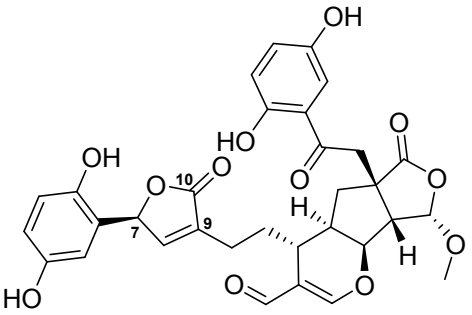
25	6	0	-3.784550	-2.096280	-0.121549
26	6	0	-2.102248	-1.897361	1.764142
27	6	0	-1.161716	-0.703209	1.420878
28	6	0	-0.823443	0.092218	2.656035
29	6	0	0.418884	0.080166	3.192385
30	6	0	-1.816562	0.942627	3.283725
31	8	0	1.463137	-0.616903	2.746855
32	8	0	-2.971383	1.072306	2.897199
33	6	0	1.233513	-1.597126	1.682473
34	6	0	2.784035	-2.927261	0.097018
35	6	0	0.134554	-1.142057	0.717490

36	6	0	0.837397	-0.050834	-0.109698
37	6	0	2.520259	-1.602757	0.852005
38	8	0	1.898905	-3.916621	0.477045
39	6	0	2.209735	-5.220351	-0.033034
40	6	0	-2.710997	-2.541730	0.549966
41	8	0	-3.485421	0.233843	-1.569676
42	1	0	-1.464141	1.499092	4.175315
43	1	0	3.369421	-1.389783	1.498179
44	1	0	-0.076642	-1.997134	0.069317
45	6	0	-4.587203	-0.872771	0.239225
46	6	0	-4.292468	-2.828824	-1.311261
47	8	0	-5.300836	-2.516709	-1.911607
48	8	0	-3.542903	-3.889852	-1.678348
49	1	0	9.136984	1.758905	-0.611310
50	1	0	8.496587	4.119296	-0.236708
51	1	0	4.381452	3.002948	-0.030291
52	1	0	3.150263	1.211100	0.690951
53	1	0	2.993453	1.354108	-1.046713
54	1	0	6.735448	5.576679	0.108918
55	1	0	6.746106	-0.809473	-0.755367
56	1	0	-5.891929	4.384545	-2.296497
57	1	0	-7.703559	4.502126	-0.614649
58	1	0	-6.510496	0.725049	0.976836
59	1	0	-3.678690	1.659797	-2.439927
60	1	0	-8.703820	3.433019	1.176316
61	1	0	-2.886687	-1.522532	2.423902
62	1	0	-1.540425	-2.645298	2.329970
63	1	0	-1.714148	-0.045525	0.743451
64	1	0	0.682181	0.687307	4.052880
65	1	0	1.029523	-2.546576	2.172459
66	1	0	3.818888	-3.261363	0.202490
67	1	0	0.362127	0.115193	-1.077329
68	1	0	0.821260	0.901288	0.427226
69	1	0	1.500053	-5.907284	0.423723
70	1	0	2.102763	-5.249375	-1.119746
71	1	0	3.229577	-5.506838	0.244401
72	1	0	-2.233698	-3.442211	0.180218
73	1	0	-5.646557	-1.132460	0.295093
74	1	0	-4.297664	-0.485206	1.220585
75	1	0	-3.974678	-4.290676	-2.447738



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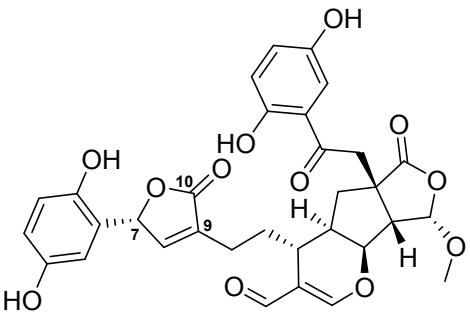

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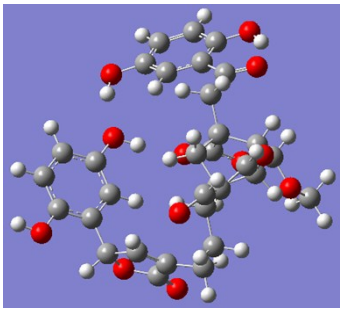

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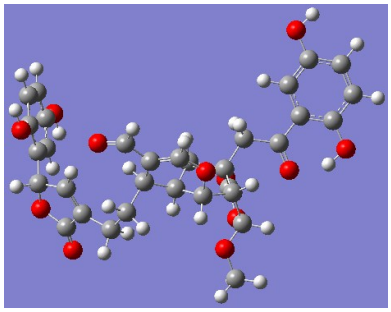

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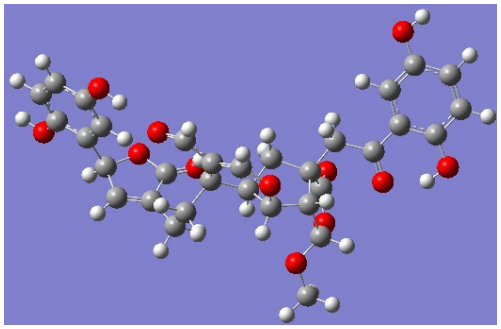

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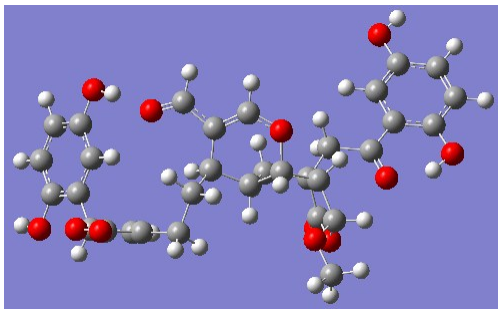
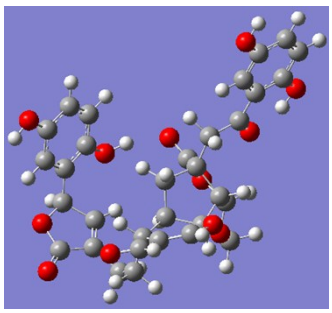
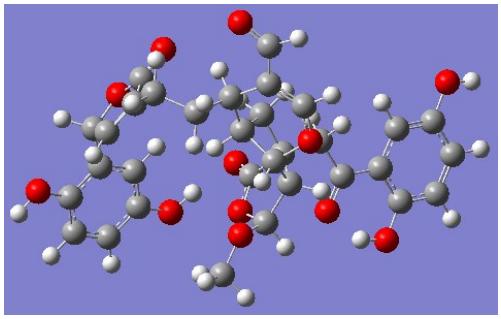


(7*R*13*R*9'*R*12'*R*13'*S*14'*S*15'*S*)-2a



(7*R*13*R*9'*R*12'*R*13'*S*14'*S*15'*S*)-2b



(7*R*13*R*9'*R*12'*R*13'*S*14'*S*15'*S*)-2c

Figure S2. Optimized geometries of predominant conformers for compound **2** at the B3LYP/6-31G (d,p) level in MeOH.

Table S2. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **2** at B3LYP/6-311G (d,p) level in MeOH.

conformer	E+ZPE	G	%
(7*S*13*R*)-2a	–2140.164726	–2140.236545	0.0
(7*S*13*R*)-2b	–2140.165432	–2140.241178	0.1
(7*S*13*R*)-2c	–2140.171605	–2140.247716	99.9

conformer	E+ZPE	G	%
(7*R*13*R*)-2a	–2140.170596	–2140.245894	98.4
(7*R*13*R*)-2b	–2140.165101	–2140.238773	0.1
(7*R*13*R*)-2c	–2140.169049	–2140.241954	1.5

E+ZPE, G: total energy with zero point energy (ZPE) and Gibbs free energy at 298.15 K, %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors

Standard orientation of (7*S*13*R*)-2a at B3LYP/6-311 G (d,p) level in MeOH:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.365900	1.469262	0.141953
2	6	0	-5.702079	2.682923	0.095351
3	6	0	-4.360863	2.749886	-0.318097
4	6	0	-3.725614	1.588700	-0.717958
5	6	0	-4.367029	0.332005	-0.652339
6	6	0	-5.712627	0.278071	-0.203637
7	6	0	-3.663962	-0.908857	-0.994626
8	6	0	-2.239726	-0.871794	-1.529823
9	8	0	-4.202656	-2.016927	-0.849253
10	6	0	-1.132537	-1.257515	-0.510366
11	8	0	-3.738283	3.966119	-0.311213
12	8	0	-6.395524	-0.877362	-0.092969
13	6	0	-1.336638	-0.574567	0.848595
14	8	0	-1.259787	0.609883	1.095755
15	8	0	-1.615112	-1.459640	1.805806
16	6	0	2.060575	4.771468	-1.316628

17	6	0	0.722138	4.463119	-1.100846
18	6	0	0.380316	3.428662	-0.229982
19	6	0	1.385591	2.724491	0.429326
20	6	0	2.732449	3.026179	0.216803
21	6	0	3.071516	4.054450	-0.670556
22	8	0	4.402235	4.311607	-0.871790
23	8	0	-0.950529	3.138074	-0.040023
24	6	0	3.819003	2.245727	0.934592
25	6	0	4.019771	0.845155	0.418439
26	8	0	3.469159	2.053961	2.326379
27	6	0	3.776524	-0.046211	1.384394
28	6	0	3.780058	-1.545362	1.429829
29	6	0	3.446805	0.720343	2.615636
30	6	0	3.744605	-2.309500	0.095558
31	6	0	2.631055	-1.913949	-0.907577
32	6	0	2.622717	-2.834467	-2.103831
33	6	0	1.600774	-3.688709	-2.340193
34	6	0	3.677789	-2.776007	-3.098796
35	8	0	3.191970	0.310200	3.721321
36	8	0	0.508127	-3.850916	-1.592869
37	8	0	4.625984	-2.003133	-3.070271
38	6	0	0.434974	-3.161274	-0.305809
39	6	0	-1.584013	-2.852448	1.309270
40	6	0	1.214223	-1.839228	-0.314913
41	6	0	0.263385	-0.891142	-1.057622
42	6	0	-1.047989	-2.767579	-0.130610
43	8	0	-0.777595	-3.605035	2.122303
44	6	0	-1.329773	-3.897758	3.416556
45	1	0	-7.396679	1.414316	0.470179
46	1	0	-6.206376	3.595754	0.390368
47	1	0	-2.702184	1.658013	-1.052528
48	1	0	-2.192301	-1.596804	-2.344951
49	1	0	-1.999942	0.101604	-1.951572
50	1	0	-2.775305	3.835360	-0.360317
51	1	0	-5.768569	-1.597418	-0.337006
52	1	0	2.324575	5.573814	-1.997814
53	1	0	-0.058447	5.015164	-1.610320
54	1	0	1.116643	1.939442	1.126003
55	1	0	4.502188	5.072482	-1.455033
56	1	0	-1.040789	2.285731	0.428280
57	1	0	4.751032	2.813887	0.906429
58	1	0	4.310487	0.660075	-0.605966
59	1	0	4.671908	-1.867758	1.980842
60	1	0	2.943853	-1.850392	2.067774

61	1	0	4.699532	-2.193111	-0.422803
62	1	0	3.653141	-3.373751	0.334634
63	1	0	2.871796	-0.916214	-1.284130
64	1	0	1.572670	-4.321036	-3.221920
65	1	0	3.572758	-3.497618	-3.934575
66	1	0	0.779061	-3.869519	0.444305
67	1	0	-2.624542	-3.184696	1.347989
68	1	0	1.273192	-1.514427	0.727723
69	1	0	0.498731	0.161607	-0.899265
70	1	0	0.292410	-1.080959	-2.134235
71	1	0	-1.660347	-3.397200	-0.772988
72	1	0	-0.633033	-4.580111	3.898370
73	1	0	-1.425181	-2.986635	4.010731
74	1	0	-2.307326	-4.378684	3.313827

Standard orientation of (7*S*13*R*)-2b at B3LYP/6-311G (d,p) level in MeOH:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	7.936204	1.909982	-0.364555
2	6	0	7.622666	3.155931	0.150637
3	6	0	6.295385	3.484435	0.467770
4	6	0	5.297822	2.547348	0.261003
5	6	0	5.592329	1.270923	-0.261715
6	6	0	6.938468	0.952068	-0.580146
7	6	0	4.538789	0.270445	-0.484141
8	6	0	3.096508	0.600909	-0.146650
9	8	0	4.807424	-0.845499	-0.949957
10	6	0	2.104652	-0.550168	-0.361755
11	8	0	5.935761	4.702008	0.978440
12	8	0	7.309346	-0.240959	-1.085480
13	6	0	2.144665	-1.037782	-1.810378
14	8	0	2.022990	-0.361969	-2.799427
15	8	0	2.290313	-2.376014	-1.872999
16	6	0	-5.743565	3.665552	0.265280
17	6	0	-5.418984	4.090619	-1.019564
18	6	0	-5.223683	3.153393	-2.033250
19	6	0	-5.355228	1.792370	-1.752231
20	6	0	-5.678152	1.360905	-0.466749
21	6	0	-5.874124	2.306935	0.547389
22	8	0	-6.190693	1.826987	1.793842
23	8	0	-4.911987	3.622169	-3.282711

24	6	0	-5.820818	-0.109164	-0.122018
25	6	0	-4.652635	-0.681722	0.636813
26	8	0	-5.904632	-0.921033	-1.309622
27	6	0	-4.137398	-1.715392	-0.035727
28	6	0	-3.002355	-2.644619	0.273664
29	6	0	-4.930350	-1.882537	-1.277234
30	6	0	-2.205127	-2.312048	1.541916
31	6	0	-1.289559	-1.066869	1.426569
32	6	0	-0.868429	-0.560873	2.785486
33	6	0	0.399092	-0.702700	3.238905
34	6	0	-1.793442	0.154091	3.642829
35	8	0	-4.811215	-2.696371	-2.160093
36	8	0	1.405971	-1.293798	2.597349
37	8	0	-2.960937	0.405217	3.369583
38	6	0	1.102655	-2.007133	1.355238
39	6	0	2.546043	-2.966735	-0.563958
40	6	0	-0.033517	-1.336760	0.576810
41	6	0	0.651071	-0.094439	-0.020037
42	6	0	2.346072	-1.839660	0.476519
43	8	0	1.675123	-4.016858	-0.353182
44	6	0	1.936376	-5.176819	-1.154690
45	1	0	8.959395	1.654231	-0.610761
46	1	0	8.411626	3.883788	0.309572
47	1	0	4.281636	2.821405	0.510414
48	1	0	3.038220	0.934155	0.893368
49	1	0	2.788019	1.454922	-0.759335
50	1	0	6.716528	5.259293	1.075113
51	1	0	6.488672	-0.776946	-1.172994
52	1	0	-5.897348	4.395218	1.053640
53	1	0	-5.318659	5.145591	-1.243722
54	1	0	-5.220997	1.059493	-2.539199
55	1	0	-6.298089	2.561793	2.408443
56	1	0	-4.802670	2.879050	-3.886961
57	1	0	-6.747572	-0.258610	0.442189
58	1	0	-4.320787	-0.266084	1.579484
59	1	0	-3.414530	-3.656371	0.365960
60	1	0	-2.345992	-2.691560	-0.603208
61	1	0	-2.900674	-2.165670	2.371982
62	1	0	-1.590680	-3.177891	1.807745
63	1	0	-1.863614	-0.268556	0.945390
64	1	0	0.717234	-0.301707	4.196158
65	1	0	-1.370976	0.485342	4.612864
66	1	0	0.902345	-3.040327	1.630172
67	1	0	3.581568	-3.313040	-0.600508

68	1	0	-0.287758	-2.024276	-0.235020
69	1	0	0.131644	0.295156	-0.896601
70	1	0	0.688303	0.709992	0.719453
71	1	0	3.230460	-1.780813	1.107864
72	1	0	1.247000	-5.947406	-0.815378
73	1	0	1.762030	-4.967115	-2.212462
74	1	0	2.967362	-5.517006	-1.011798

Standard orientation of (7*S*13*R*)-2c at B3LYP/6-311G (d,p) level in MeOH:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.156147	-1.832610	-0.568300
2	6	0	-7.805926	-3.171097	-0.612227
3	6	0	-6.456604	-3.557432	-0.597882
4	6	0	-5.474153	-2.584141	-0.538546
5	6	0	-5.805825	-1.214095	-0.491653
6	6	0	-7.174218	-0.836751	-0.508113
7	6	0	-4.768303	-0.174896	-0.429764
8	6	0	-3.302423	-0.567488	-0.418579
9	8	0	-5.070253	1.025911	-0.391898
10	6	0	-2.322139	0.607189	-0.296664
11	8	0	-6.060646	-4.866607	-0.639865
12	8	0	-7.581051	0.447448	-0.468458
13	6	0	-2.532588	1.607356	-1.433861
14	8	0	-2.548786	1.362365	-2.612429
15	8	0	-2.659541	2.864174	-0.963623
16	6	0	7.955005	-2.252491	-0.806587
17	6	0	7.235096	-2.989961	0.127913
18	6	0	6.013830	-2.510109	0.611833
19	6	0	5.539589	-1.287004	0.141273
20	6	0	6.255630	-0.537553	-0.794399
21	6	0	7.475565	-1.026093	-1.276868
22	8	0	8.157798	-0.273647	-2.199055
23	8	0	5.334322	-3.252183	1.532874
24	6	0	5.685619	0.778756	-1.281783
25	6	0	5.128108	1.638548	-0.185805
26	8	0	4.532661	0.542831	-2.146920
27	6	0	3.812667	1.811668	-0.344518
28	6	0	2.823078	2.516757	0.534772
29	6	0	3.429365	1.133847	-1.609794
30	6	0	2.210870	1.616187	1.635076

31	6	0	1.271052	0.491645	1.133749
32	6	0	0.994092	-0.526191	2.216745
33	6	0	-0.204974	-0.583865	2.849789
34	6	0	1.951075	-1.547007	2.566249
35	8	0	2.347571	1.076441	-2.146631
36	8	0	-1.249037	0.205313	2.631443
37	8	0	3.051902	-1.682438	2.031761
38	6	0	-1.087516	1.336292	1.710510
39	6	0	-2.741440	2.904821	0.491575
40	6	0	-0.070134	1.034932	0.606989
41	6	0	-0.846729	0.098460	-0.334666
42	6	0	-2.433708	1.473493	0.992251
43	8	0	-1.833247	3.822957	0.979812
44	6	0	-2.171071	5.191454	0.716582
45	1	0	-9.196542	-1.531967	-0.580128
46	1	0	-8.583240	-3.926786	-0.658541
47	1	0	-4.440652	-2.903075	-0.530338
48	1	0	-3.124790	-1.270318	0.400554
49	1	0	-3.087110	-1.114631	-1.342686
50	1	0	-6.833763	-5.441021	-0.682996
51	1	0	-6.767232	0.999651	-0.433601
52	1	0	8.900841	-2.634271	-1.177863
53	1	0	7.615640	-3.938040	0.489441
54	1	0	4.596712	-0.914208	0.519725
55	1	0	8.978330	-0.720247	-2.435691
56	1	0	4.517370	-2.783255	1.791668
57	1	0	6.427076	1.306649	-1.883348
58	1	0	5.746444	2.008100	0.621516
59	1	0	3.323261	3.354060	1.027692
60	1	0	2.035039	2.944395	-0.091232
61	1	0	3.028137	1.164049	2.202726
62	1	0	1.661787	2.254486	2.335274
63	1	0	1.772406	-0.033606	0.316040
64	1	0	-0.424090	-1.338088	3.599132
65	1	0	1.638813	-2.244683	3.364283
66	1	0	-0.836405	2.197531	2.324969
67	1	0	-3.767530	3.205923	0.715562
68	1	0	0.102803	1.983197	0.092024
69	1	0	-0.440262	0.097253	-1.346346
70	1	0	-0.809071	-0.930461	0.033372
71	1	0	-3.233409	1.152743	1.656878
72	1	0	-1.432341	5.796997	1.237899
73	1	0	-2.131320	5.403498	-0.354228
74	1	0	-3.170888	5.419892	1.100374

Standard orientation of (7*R*13*R*)-2a at B3LYP/6-311G (d,p) level in MeOH:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	8.124955	1.783240	-0.329707
2	6	0	7.791976	3.106173	-0.094659
3	6	0	6.447933	3.495510	0.015381
4	6	0	5.453548	2.540957	-0.110113
5	6	0	5.767643	1.186731	-0.347894
6	6	0	7.130607	0.806648	-0.461417
7	6	0	4.717220	0.167626	-0.481877
8	6	0	3.257640	0.564677	-0.357278
9	8	0	5.002289	-1.017969	-0.699783
10	6	0	2.262584	-0.599799	-0.453917
11	8	0	6.068733	4.790081	0.244326
12	8	0	7.520787	-0.462622	-0.691616
13	6	0	2.430216	-1.347470	-1.777051
14	8	0	2.421313	-0.865468	-2.880275
15	8	0	2.548156	-2.674961	-1.577999
16	6	0	-6.560539	3.333222	-1.498723
17	6	0	-5.933528	3.822520	-0.357360
18	6	0	-5.187153	2.964314	0.456401
19	6	0	-5.089402	1.620147	0.103018
20	6	0	-5.714628	1.119291	-1.040010
21	6	0	-6.460259	1.983328	-1.850048
22	8	0	-7.066507	1.466010	-2.966964
23	8	0	-4.582990	3.473095	1.569255
24	6	0	-5.599033	-0.358122	-1.354781
25	6	0	-4.194086	-0.889508	-1.308995
26	8	0	-6.291292	-1.137393	-0.333551
27	6	0	-4.069374	-1.802571	-0.341537
28	6	0	-2.885270	-2.573884	0.153911
29	6	0	-5.409943	-1.977246	0.277210
30	6	0	-2.213224	-1.937027	1.396251
31	6	0	-1.290388	-0.734210	1.079475
32	6	0	-0.954808	0.065348	2.317931
33	6	0	0.261339	-0.026453	2.913787
34	6	0	-1.856080	1.049863	2.864216
35	8	0	-5.745333	-2.725694	1.164021
36	8	0	1.275287	-0.787104	2.522261
37	8	0	-2.960968	1.324612	2.396168
38	6	0	1.067465	-1.706432	1.398162

39	6	0	2.658274	-3.015501	-0.164126
40	6	0	0.025614	-1.175516	0.409224
41	6	0	0.794598	-0.078114	-0.347913
42	6	0	2.390966	-1.712695	0.626753
43	8	0	1.740322	-3.998581	0.146426
44	6	0	2.044798	-5.290381	-0.397021
45	1	0	9.161067	1.480091	-0.416433
46	1	0	8.578421	3.847331	0.004810
47	1	0	4.424651	2.862925	-0.022887
48	1	0	3.107796	1.086629	0.592149
49	1	0	3.031305	1.291252	-1.144967
50	1	0	6.849408	5.352102	0.307433
51	1	0	6.700396	-1.001656	-0.759712
52	1	0	-7.137359	4.006877	-2.124586
53	1	0	-6.014497	4.870422	-0.093409
54	1	0	-4.501531	0.958906	0.726223
55	1	0	-7.555064	2.162057	-3.420274
56	1	0	-4.047607	2.776256	1.994016
57	1	0	-6.086829	-0.576685	-2.305831
58	1	0	-3.424242	-0.525840	-1.976409
59	1	0	-3.225818	-3.576102	0.427814
60	1	0	-2.160320	-2.695609	-0.654363
61	1	0	-2.990169	-1.620919	2.096728
62	1	0	-1.630642	-2.706500	1.912405
63	1	0	-1.826720	-0.067517	0.395795
64	1	0	0.523338	0.571136	3.781297
65	1	0	-1.489454	1.589503	3.756484
66	1	0	0.817103	-2.670910	1.833074
67	1	0	3.681936	-3.373243	-0.031560
68	1	0	-0.177186	-2.001616	-0.277840
69	1	0	0.368735	0.134830	-1.329343
70	1	0	0.782314	0.856236	0.219400
71	1	0	3.213860	-1.545347	1.318695
72	1	0	1.302098	-5.976526	0.005099
73	1	0	1.982957	-5.278691	-1.487549
74	1	0	3.045718	-5.609447	-0.088200

Standard orientation of (7*R*13*R*)-2b at B3LYP/6-311G (d,p) level in MeOH:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	7.353019	0.764940	-0.115611

2	6	0	7.349956	1.609834	0.980881
3	6	0	6.154426	1.896509	1.658615
4	6	0	4.973430	1.323069	1.220601
5	6	0	4.951231	0.458035	0.106722
6	6	0	6.166452	0.178679	-0.571768
7	6	0	3.701152	-0.152178	-0.364522
8	6	0	2.396555	0.143537	0.351627
9	8	0	3.687784	-0.904214	-1.349077
10	6	0	1.180267	-0.621862	-0.185881
11	8	0	6.099444	2.725342	2.745684
12	8	0	6.236892	-0.632288	-1.645688
13	6	0	0.967186	-0.357880	-1.675831
14	8	0	0.838470	0.728826	-2.197503
15	8	0	0.860404	-1.493083	-2.371279
16	6	0	-1.182276	3.561378	-1.470997
17	6	0	-1.533928	4.429427	-0.443735
18	6	0	-2.765488	4.282418	0.194050
19	6	0	-3.628274	3.257795	-0.195510
20	6	0	-3.271629	2.370452	-1.213231
21	6	0	-2.040875	2.533579	-1.865549
22	8	0	-1.724063	1.681005	-2.896983
23	8	0	-3.075056	5.167734	1.192345
24	6	0	-4.205360	1.234338	-1.614384
25	6	0	-3.577709	-0.128457	-1.536123
26	8	0	-5.324457	1.147523	-0.705990
27	6	0	-4.215886	-0.886283	-0.641430
28	6	0	-3.914865	-2.287176	-0.202457
29	6	0	-5.342442	-0.085398	-0.105663
30	6	0	-3.326358	-2.413331	1.224248
31	6	0	-2.158055	-1.455683	1.567976
32	6	0	-1.599400	-1.752060	2.939951
33	6	0	-0.370738	-2.295134	3.106086
34	6	0	-2.332941	-1.402310	4.143026
35	8	0	-6.186886	-0.385130	0.701445
36	8	0	0.484541	-2.642168	2.141410
37	8	0	-3.425433	-0.852840	4.163300
38	6	0	0.013614	-2.585118	0.758005
39	6	0	1.171223	-2.673123	-1.550364
40	6	0	-1.001805	-1.459698	0.554985
41	6	0	-0.115862	-0.202813	0.570720
42	6	0	1.229514	-2.178126	-0.087664
43	8	0	0.195592	-3.624549	-1.737591
44	6	0	0.232501	-4.277473	-3.015706
45	1	0	8.273758	0.542903	-0.640811

46	1	0	8.281307	2.053204	1.318127
47	1	0	4.063700	1.558110	1.756401
48	1	0	2.510210	-0.074623	1.417103
49	1	0	2.202299	1.219155	0.279681
50	1	0	6.980697	3.060867	2.946035
51	1	0	5.321383	-0.944436	-1.824719
52	1	0	-0.229988	3.676144	-1.976136
53	1	0	-0.865809	5.224620	-0.135731
54	1	0	-4.582981	3.134836	0.301010
55	1	0	-0.769718	1.491340	-2.879423
56	1	0	-3.941977	4.953726	1.555881
57	1	0	-4.616776	1.419689	-2.612935
58	1	0	-2.722919	-0.387257	-2.140434
59	1	0	-4.836294	-2.877226	-0.231935
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61	1	0	-4.115691	-2.230668	1.955909
62	1	0	-3.005629	-3.451033	1.359281
63	1	0	-2.572703	-0.442159	1.598022
64	1	0	0.050650	-2.472426	4.090557
65	1	0	-1.823798	-1.665098	5.093040
66	1	0	-0.365565	-3.575269	0.515492
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71	1	0	2.139564	-2.551692	0.378315
72	1	0	-0.518449	-5.063910	-2.980180
73	1	0	-0.006416	-3.575365	-3.817439
74	1	0	1.219146	-4.717548	-3.191414

Standard orientation of (7*R*13*R*)-2c at B3LYP/6-311G (d,p) level in MeOH:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	7.318587	-1.639269	-0.161927
2	6	0	7.773111	-0.706414	-1.078044
3	6	0	6.895161	0.240346	-1.628922
4	6	0	5.566136	0.236909	-1.243063
5	6	0	5.079538	-0.702458	-0.310038
6	6	0	5.976319	-1.658260	0.235395
7	6	0	3.669947	-0.713288	0.102356
8	6	0	2.704929	0.306001	-0.473721

9	8	0	3.246431	-1.549401	0.912583
10	6	0	1.281873	0.248768	0.099863
11	8	0	7.295704	1.179274	-2.539705
12	8	0	5.596971	-2.594106	1.127687
13	6	0	0.664025	-1.134882	-0.083944
14	8	0	0.532693	-1.724848	-1.137705
15	8	0	0.201063	-1.635107	1.061136
16	6	0	-4.603378	-4.138986	0.100904
17	6	0	-3.270906	-4.495024	-0.087651
18	6	0	-2.380148	-3.597369	-0.680275
19	6	0	-2.847539	-2.345242	-1.093687
20	6	0	-4.179986	-1.982162	-0.904671
21	6	0	-5.061864	-2.884399	-0.296734
22	8	0	-6.360551	-2.469668	-0.122923
23	8	0	-1.086682	-3.992262	-0.853952
24	6	0	-4.717468	-0.638338	-1.355134
25	6	0	-4.831353	0.409931	-0.282082
26	8	0	-3.858218	-0.030019	-2.340907
27	6	0	-4.148797	1.506849	-0.627024
28	6	0	-4.036721	2.832587	0.070303
29	6	0	-3.531852	1.238115	-1.951112
30	6	0	-2.800975	3.045732	0.971836
31	6	0	-1.431225	3.012751	0.230334
32	6	0	-0.550659	4.179978	0.604148
33	6	0	0.574748	4.028353	1.337084
34	6	0	-0.858265	5.515624	0.126560
35	8	0	-2.851428	1.955695	-2.644910
36	8	0	1.038264	2.881902	1.839195
37	8	0	-1.818152	5.801977	-0.575727
38	6	0	0.174356	1.705811	1.757126
39	6	0	0.575688	-0.804469	2.216767
40	6	0	-0.662284	1.699093	0.472012
41	6	0	0.368793	1.303723	-0.597092
42	6	0	1.128431	0.511279	1.630573
43	8	0	-0.530521	-0.598082	3.005265
44	6	0	-0.958053	-1.747384	3.752319
45	1	0	7.993223	-2.372096	0.263180
46	1	0	8.817750	-0.708528	-1.372362
47	1	0	4.907098	0.974759	-1.680229
48	1	0	3.106307	1.311350	-0.319915
49	1	0	2.657740	0.159767	-1.558272
50	1	0	8.232993	1.065992	-2.734314
51	1	0	4.634265	-2.464245	1.282012
52	1	0	-5.290382	-4.839982	0.563903

53	1	0	-2.911343	-5.467960	0.225359
54	1	0	-2.173542	-1.656497	-1.586368
55	1	0	-6.880248	-3.182988	0.264883
56	1	0	-0.520233	-3.216898	-1.041151
57	1	0	-5.695349	-0.788356	-1.825143
58	1	0	-5.427335	0.254040	0.606663
59	1	0	-4.039482	3.621274	-0.688428
60	1	0	-4.931293	2.972768	0.682666
61	1	0	-2.929644	4.018160	1.451619
62	1	0	-2.803136	2.304458	1.778192
63	1	0	-1.634535	3.096282	-0.840554
64	1	0	1.235096	4.859323	1.564233
65	1	0	-0.144556	6.303613	0.443309
66	1	0	-0.419596	1.689363	2.668601
67	1	0	1.343128	-1.380196	2.737572
68	1	0	-1.385324	0.884601	0.582627
69	1	0	-0.087486	0.911761	-1.506514
70	1	0	0.973794	2.168559	-0.882137
71	1	0	2.070592	0.749913	2.120485
72	1	0	-1.762516	-1.408629	4.401756
73	1	0	-1.327569	-2.528877	3.084948
74	1	0	-0.134031	-2.136992	4.358342

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3. Supplementary Figures

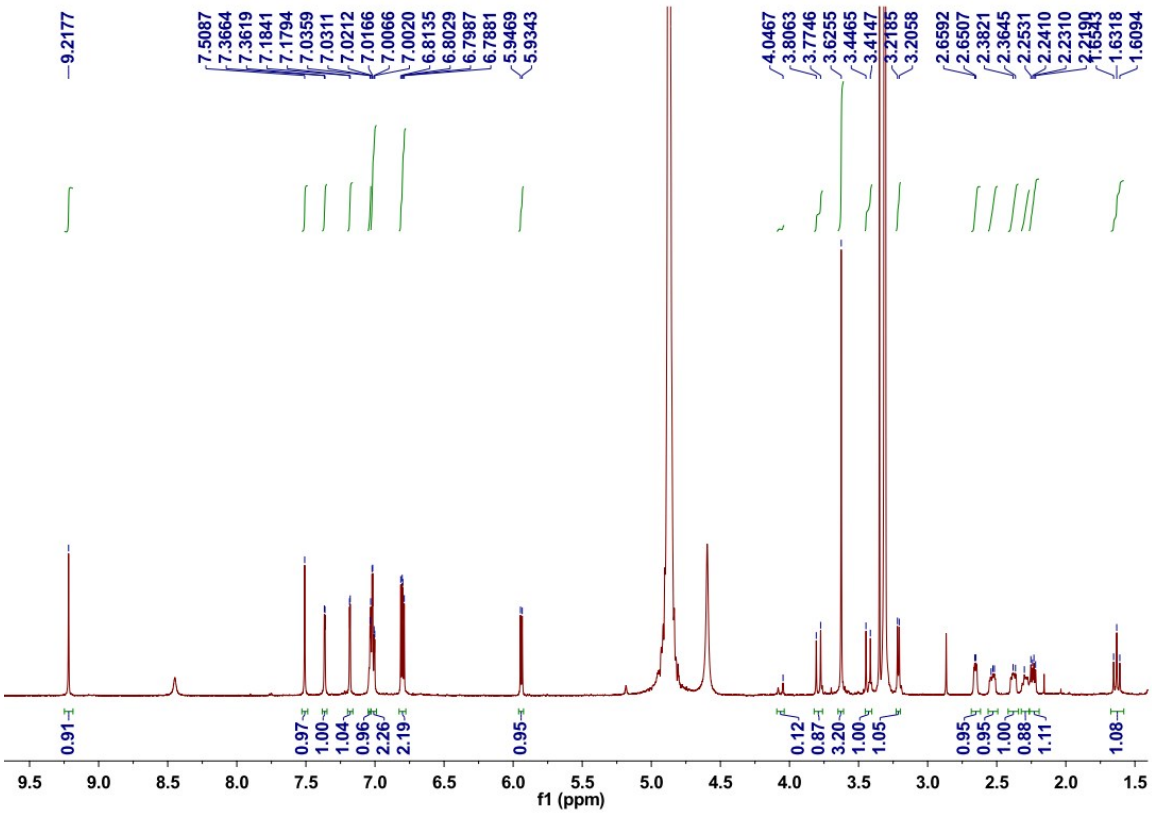


Figure S3. ^{1}H NMR spectrum of **1** in methanol-d_4

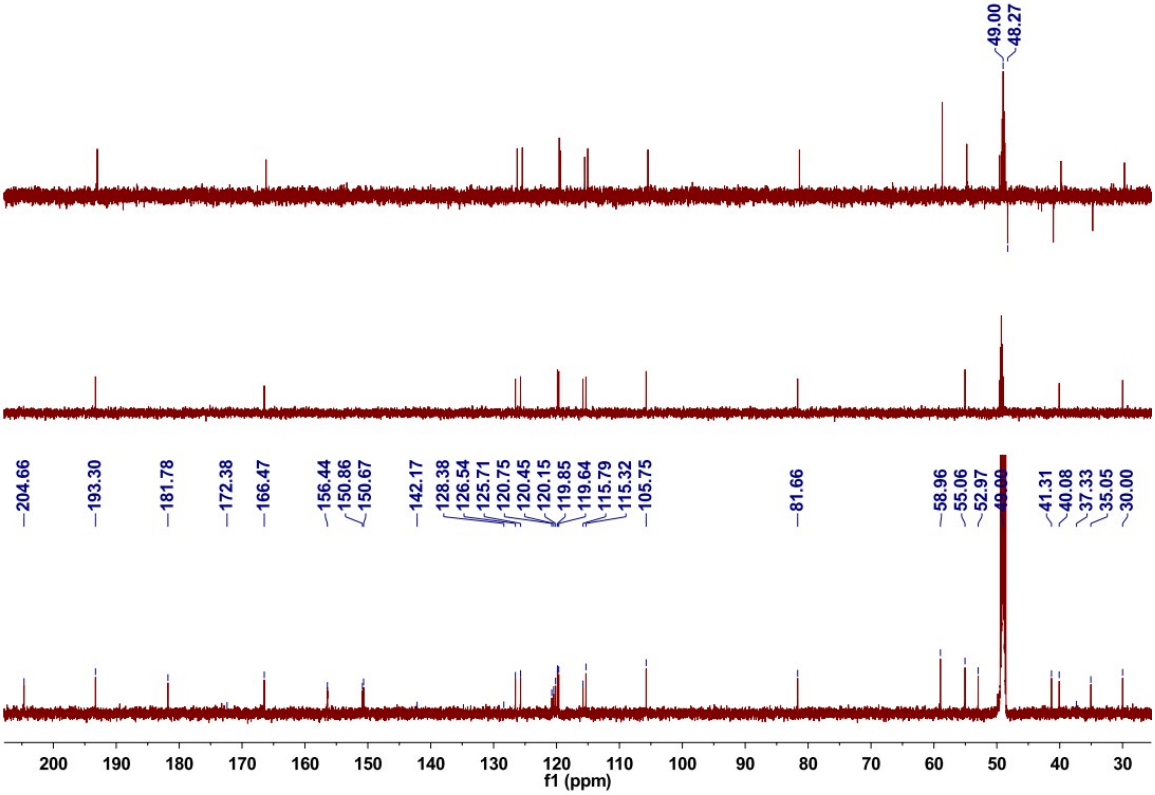


Figure S4. ^{13}C NMR and DEPT spectra of **1** in methanol-d_4

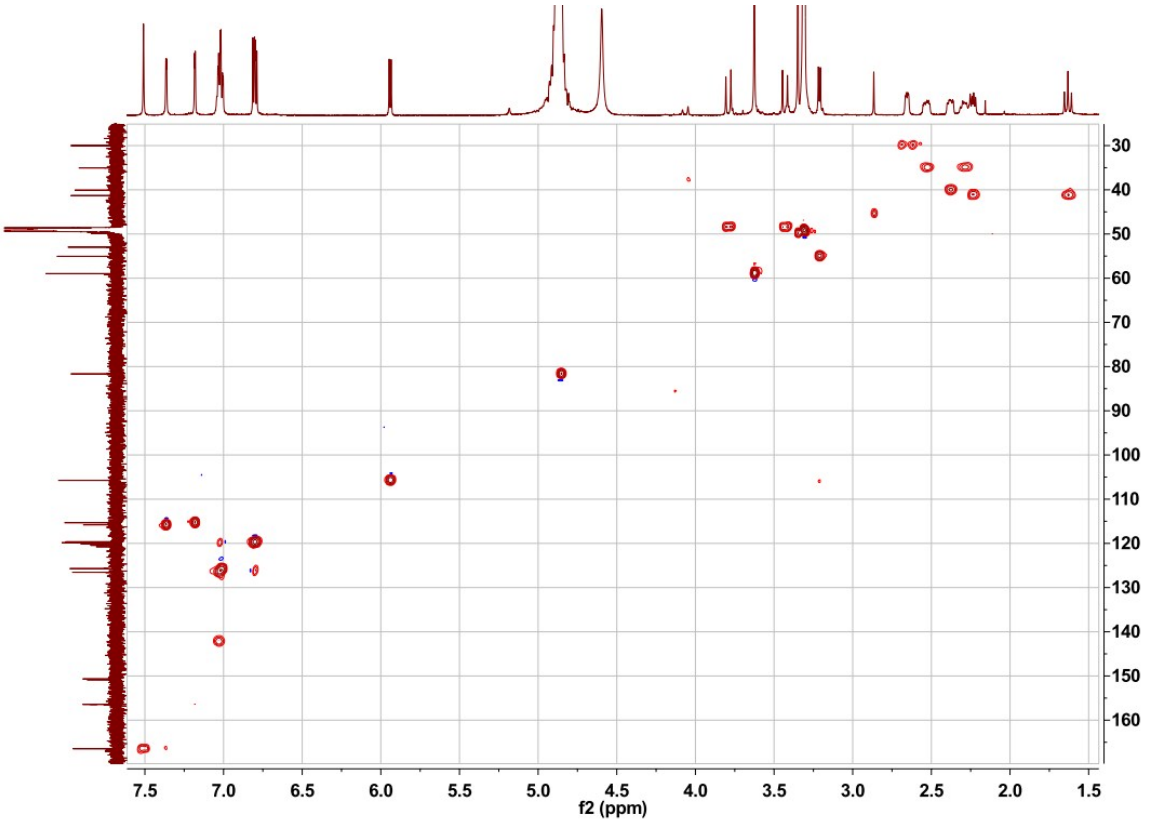
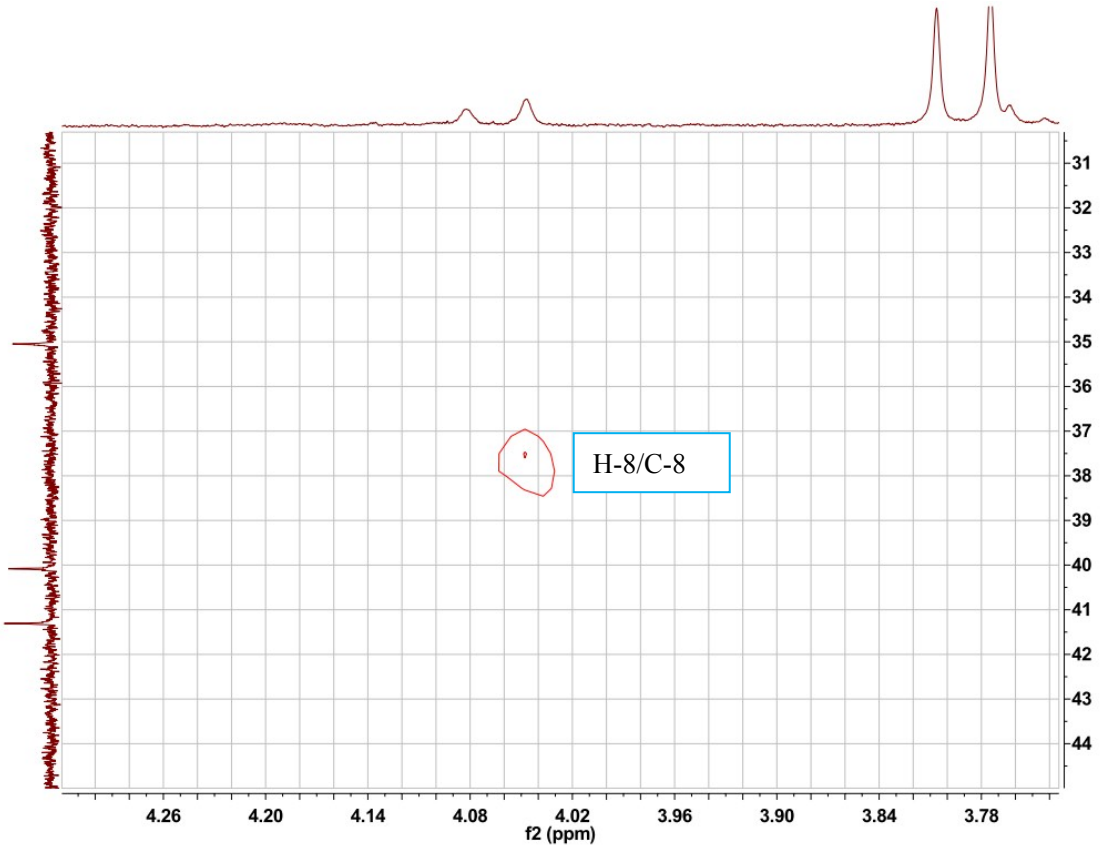


Figure S5. HSQC spectrum of **1** in methanol-d_4



Enlarged HSQC spectrum of **1** (H-8/C-8) in methanol-d_4

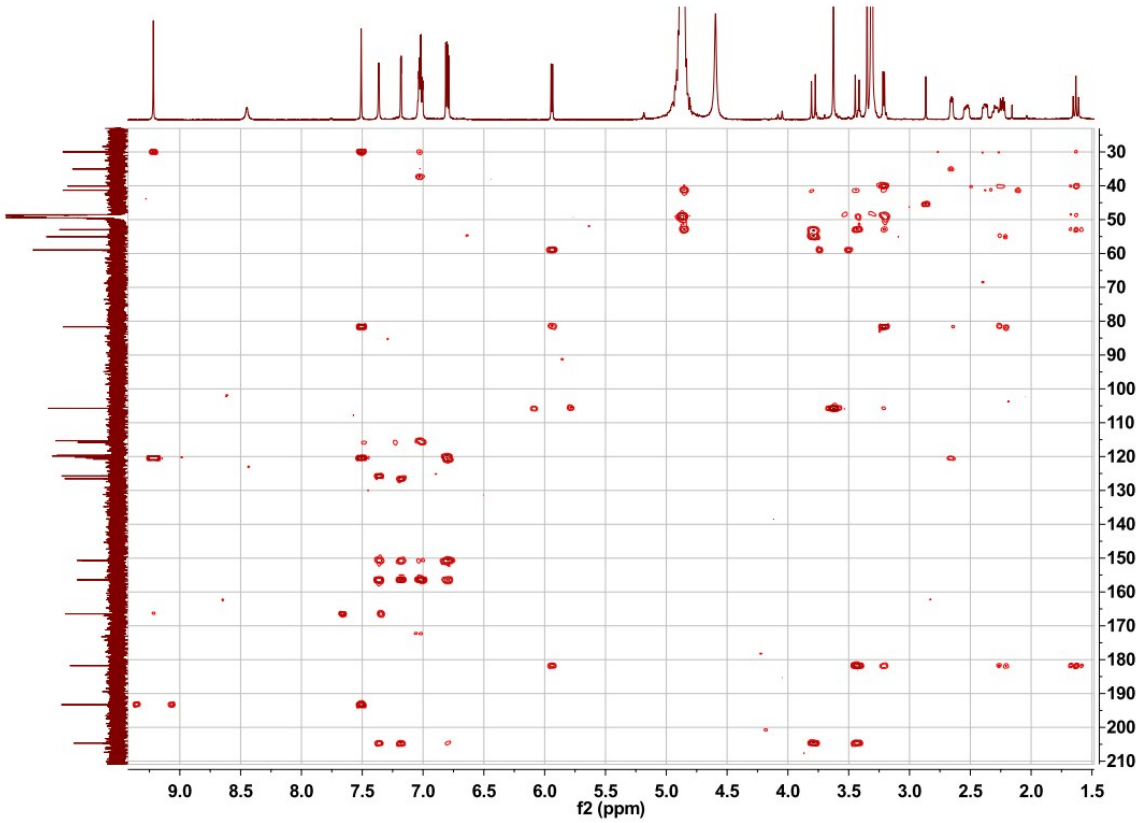
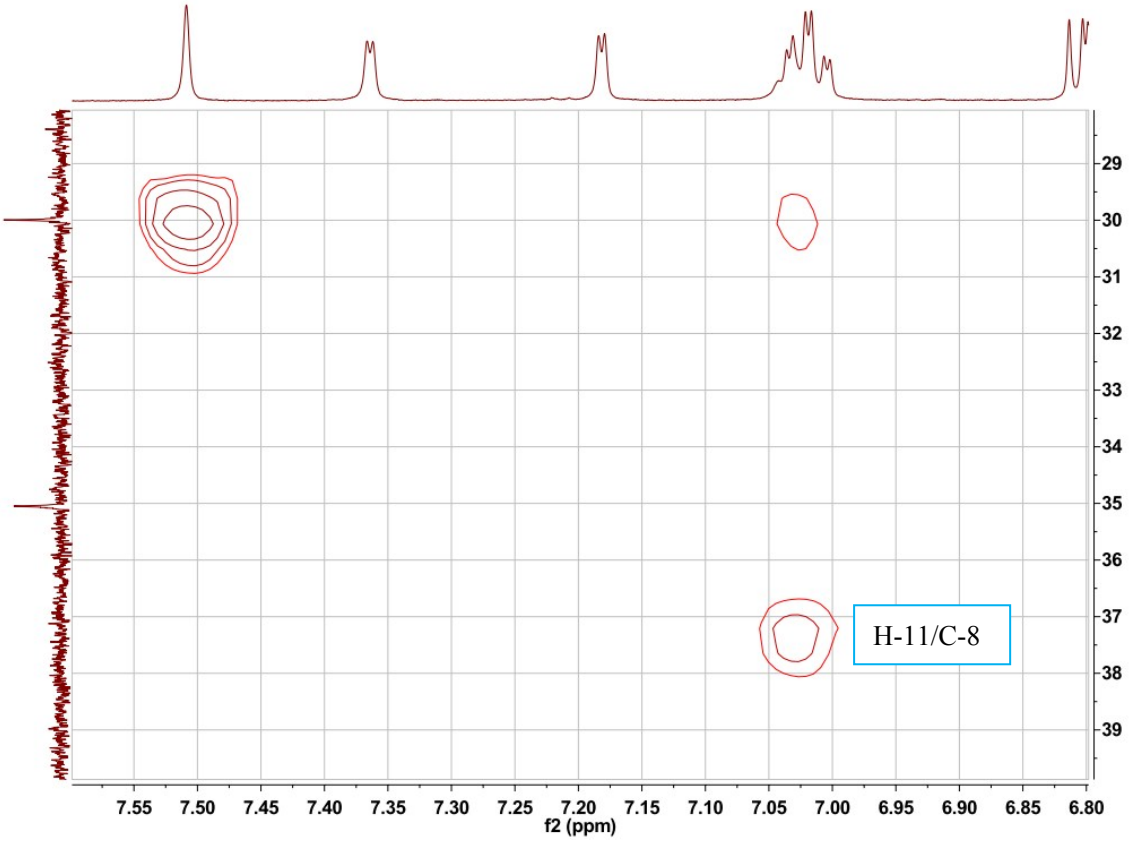


Figure S6. HMBC spectrum of **1** in methanol-d_4



Enlarged HMBC spectrum of **1** (low-field regions) in methanol-d_4

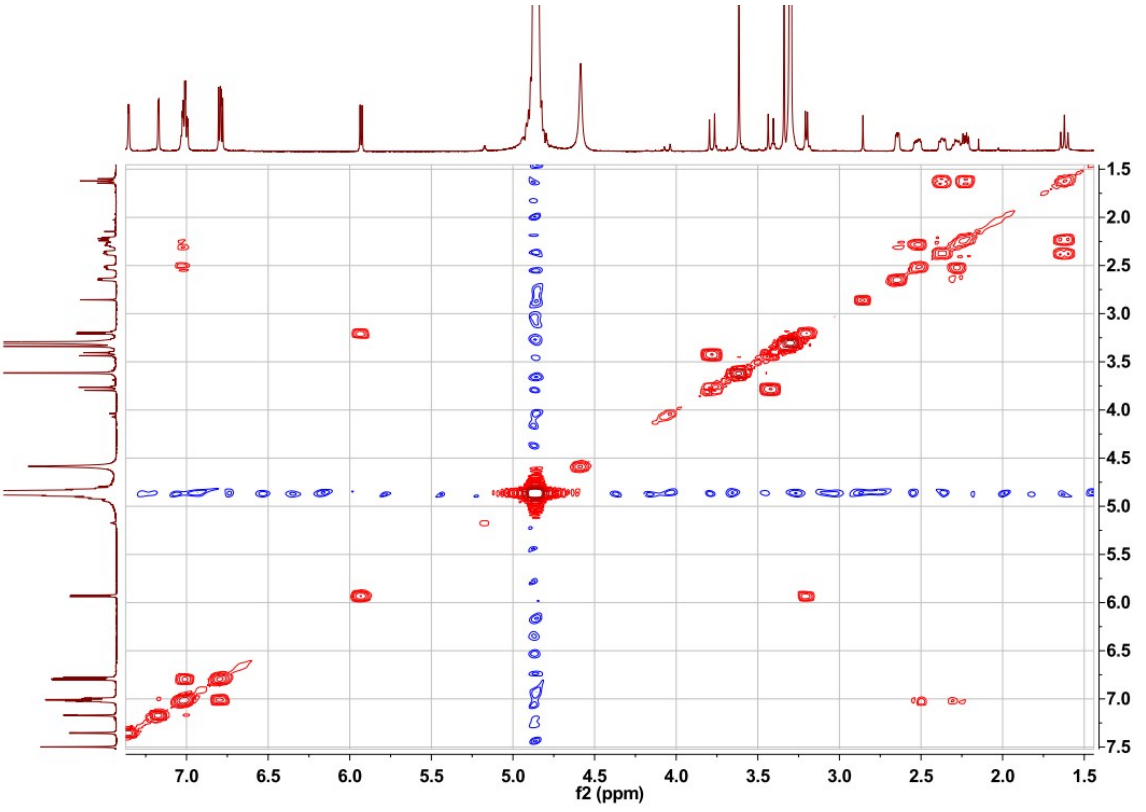


Figure S7. ^{1}H-^{1}H COSY spectrum of **1** in methanol-d_4

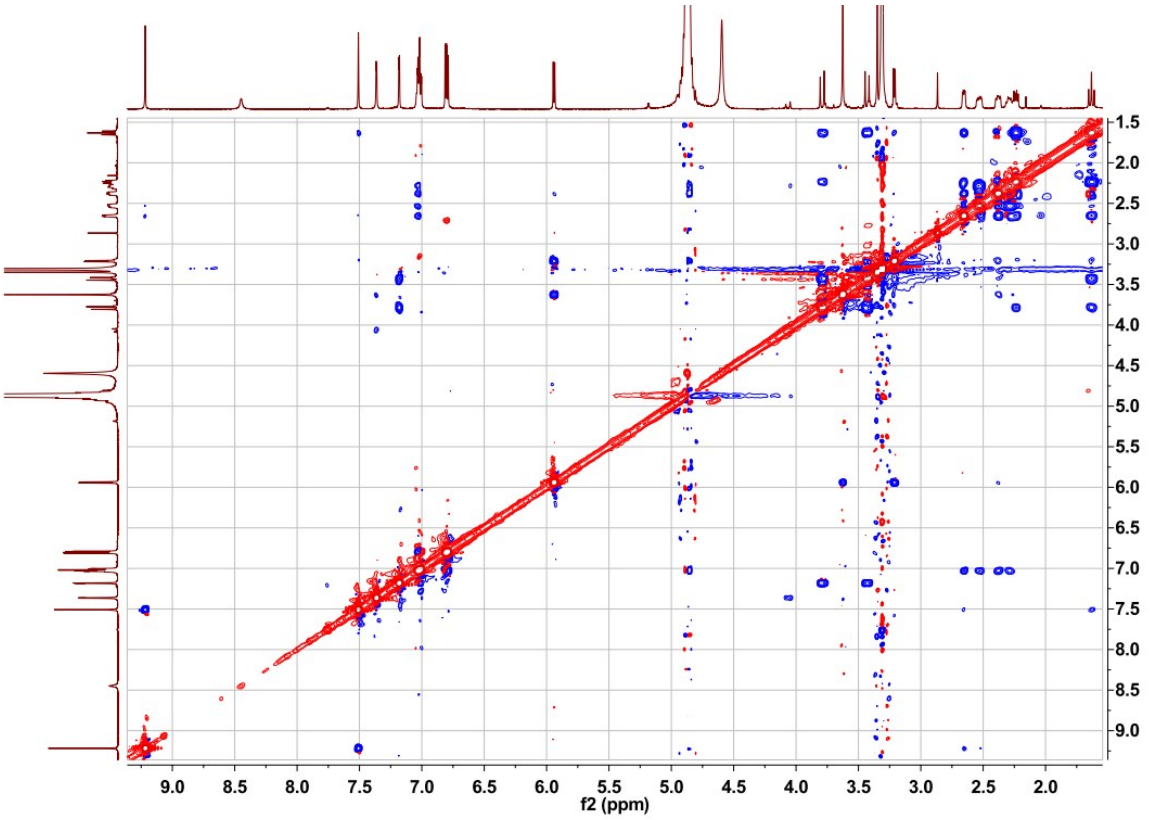
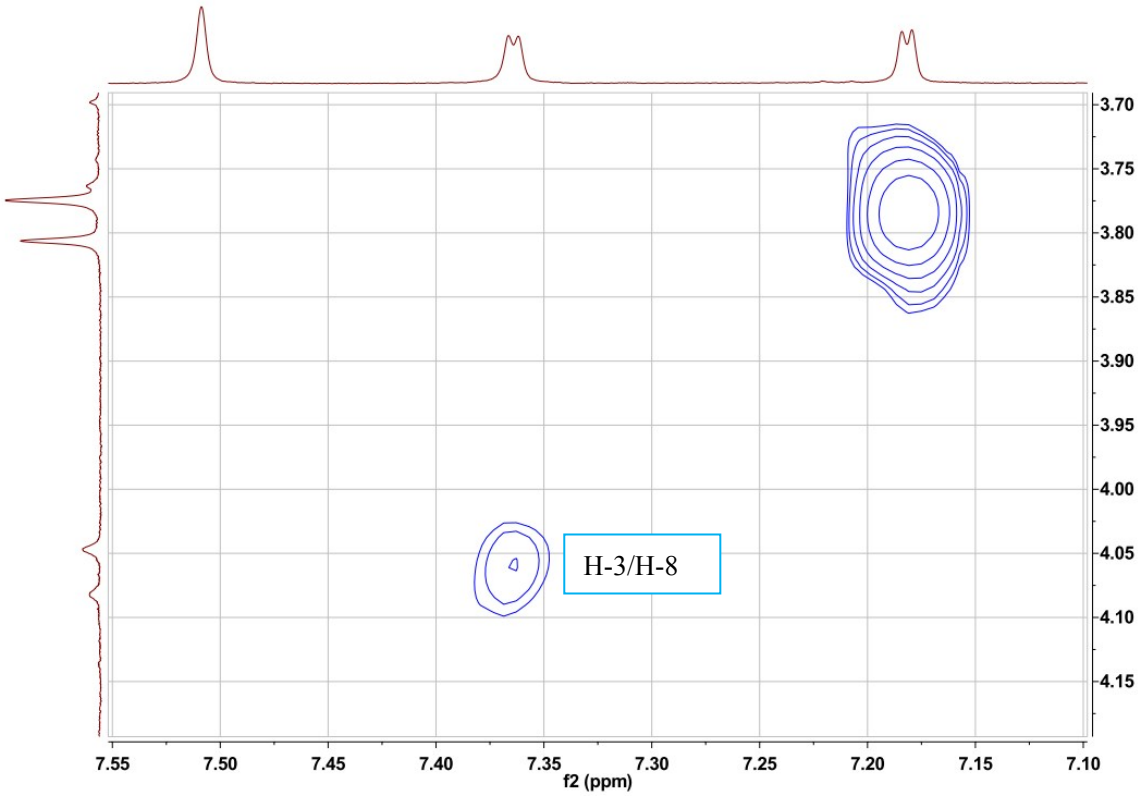


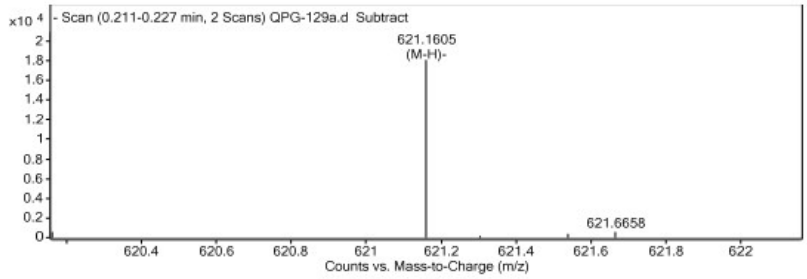
Figure S8. ROESY spectrum of **1** in methanol-d_4



Enlarged ROESY spectrum of **1** (H-3/H-8) in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
112.9855	1	17540.81		
255.2325	1	6211.53		
325.1841	1	5864.41		
339.1995	1	5671.76		
621.1605		18058.91	C32 H30 O13	(M-H)-
622.1665	1	17043.65		
623.1719	1	9391.21		
1033.9871		6052.03		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C32 H30 O13	622.1686	621.1614	621.1605	0.8	1.4	18.0000

Figure S9. HRESIMS spectrum of **1**

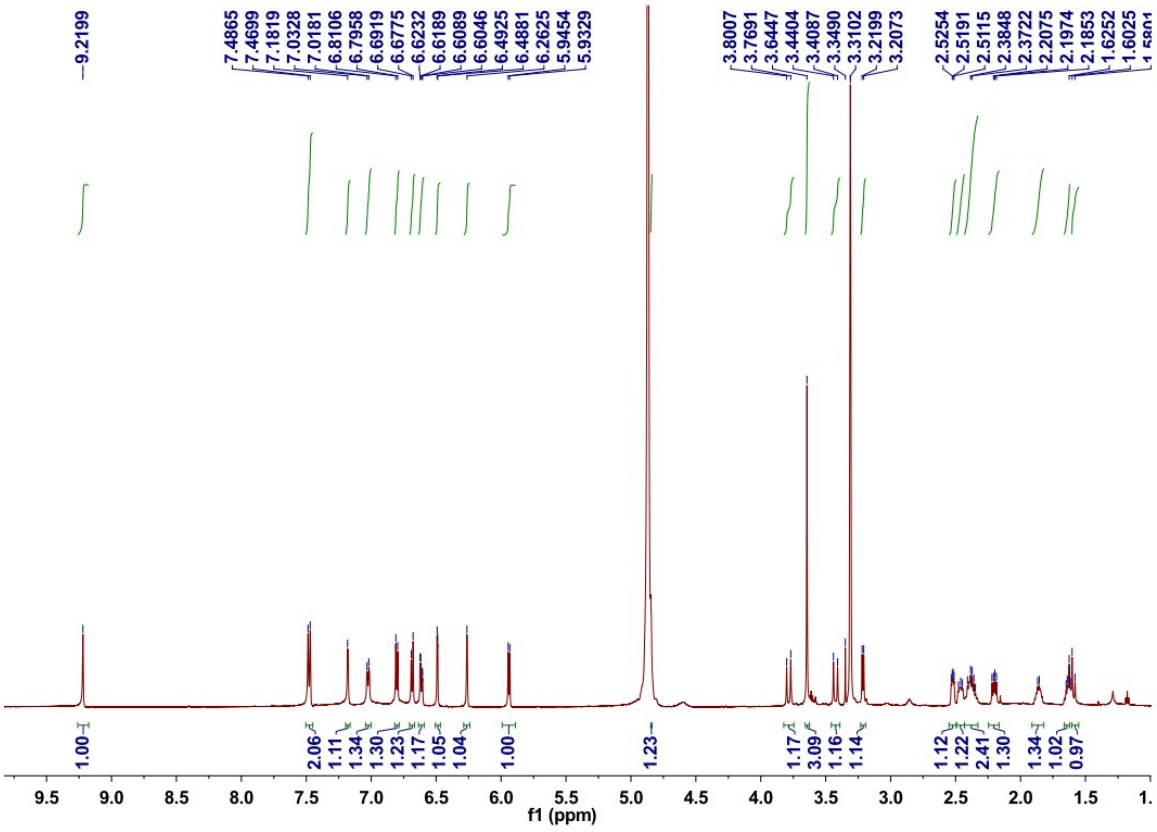


Figure S10. ^{1}H NMR spectrum of **2** in methanol-d_4

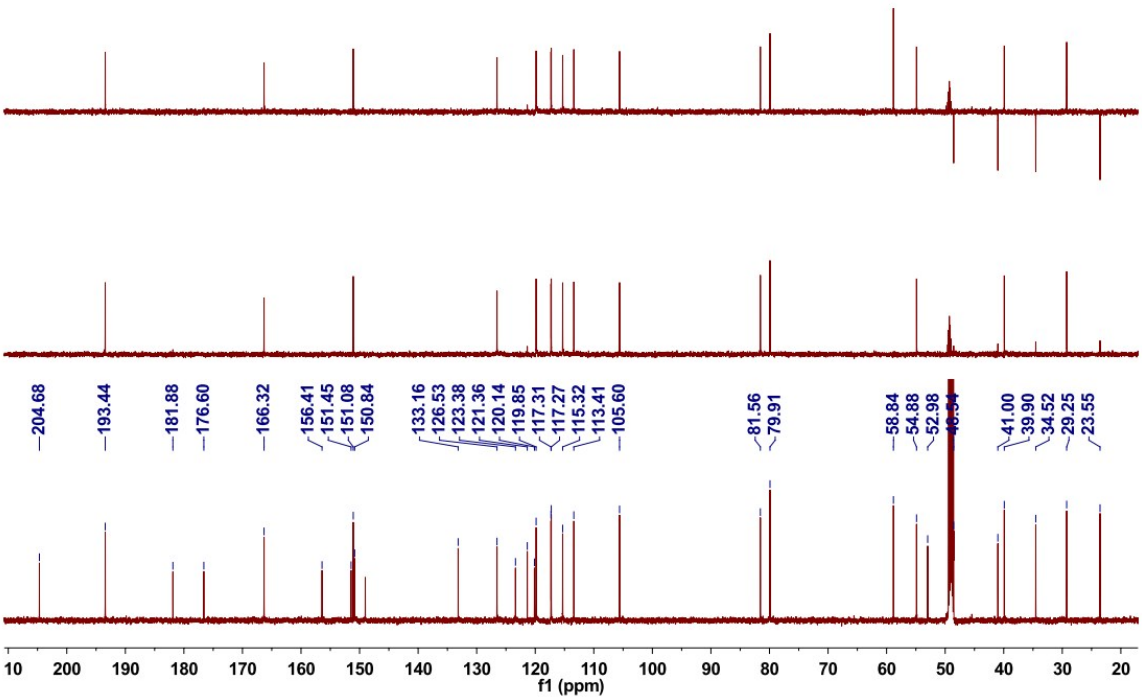


Figure S11. ^{13}C NMR and DEPT spectra of **2** in methanol-d_4

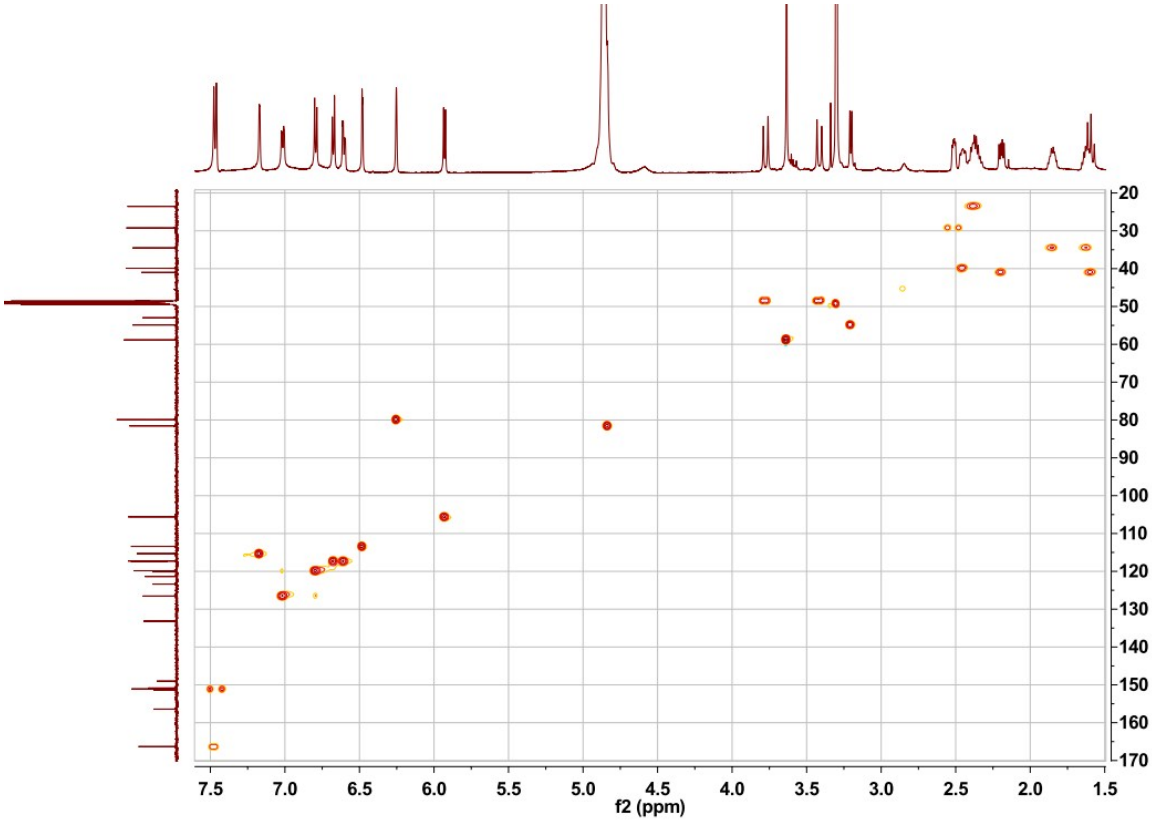


Figure S12. HSQC spectrum of **2** in methanol-d_4

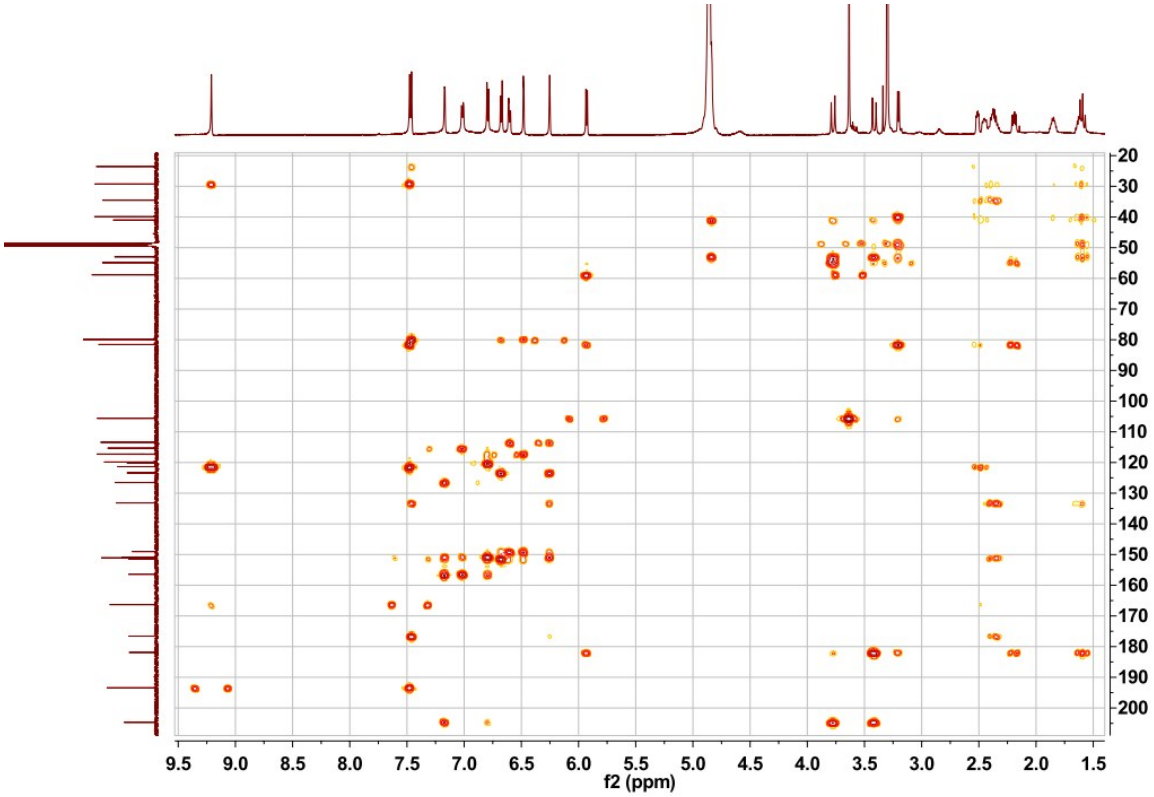
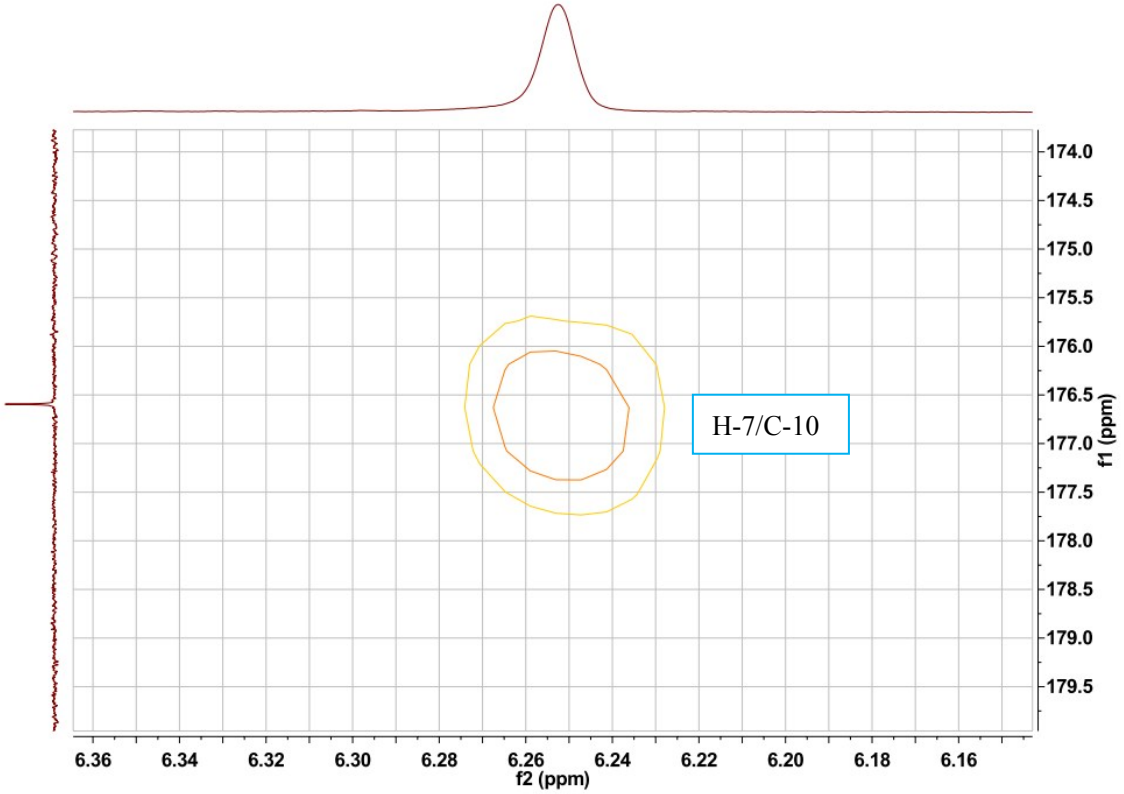


Figure S13. HMBC spectrum of **2** in methanol-d_4



Enlarged HMBC spectrum of **2** (low-field regions) in methanol-d_4

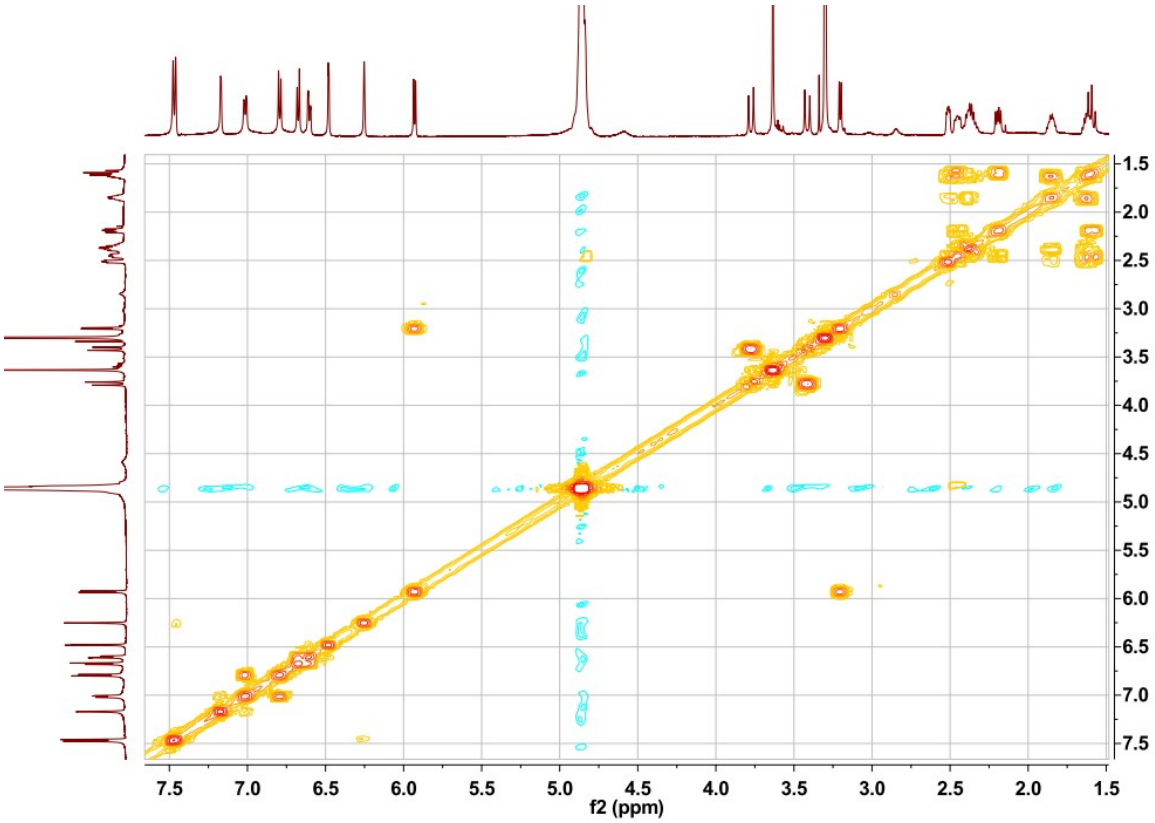


Figure S14. ^{1}H-^{1}H COSY spectrum of **2** in methanol-d_4

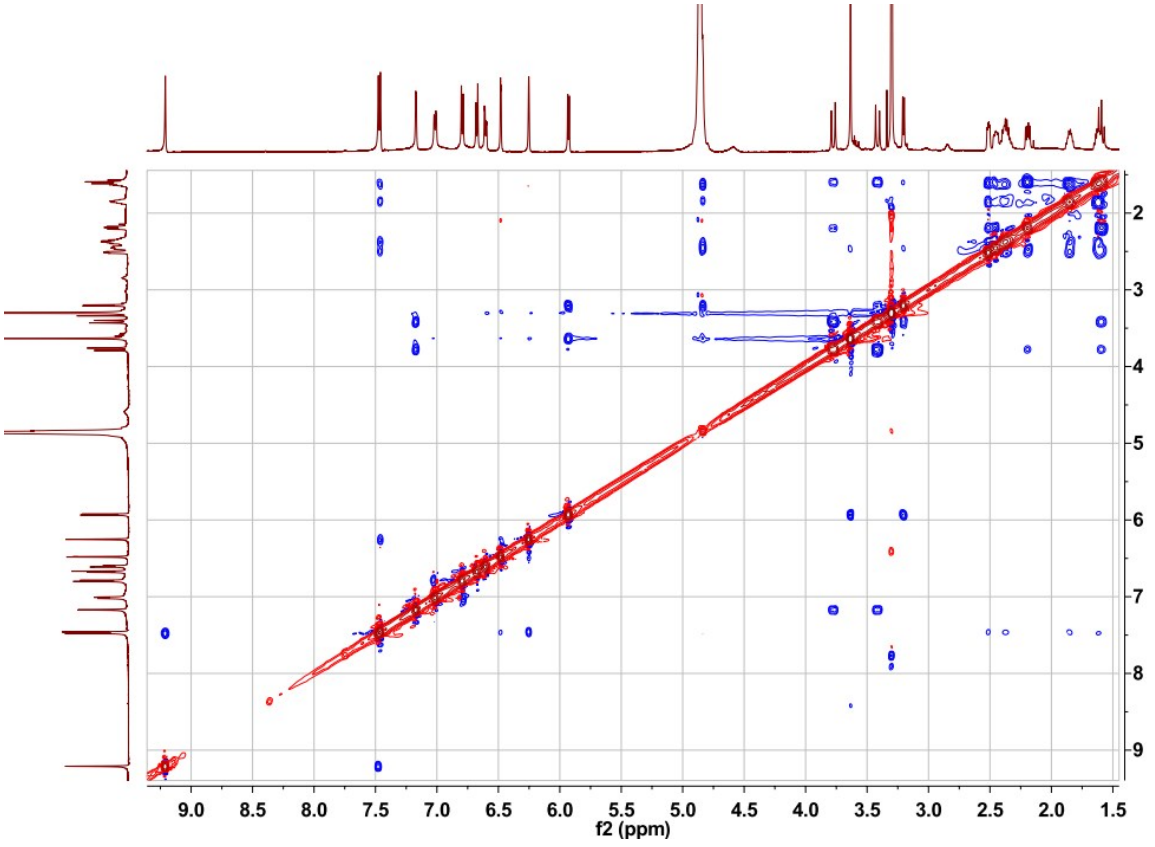
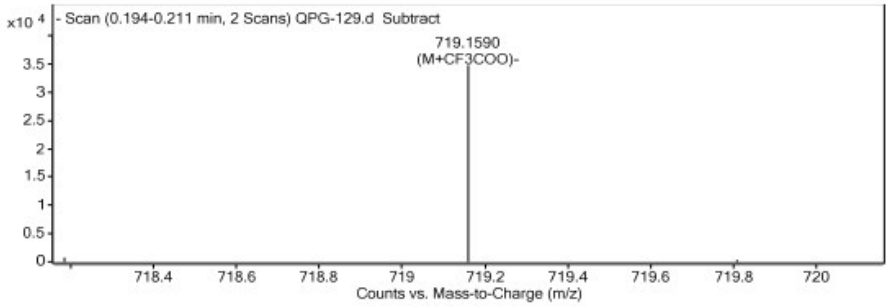


Figure S15. ROESY spectrum of **2** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
112.9855		11406.9		
605.1661	1	13353.46		
606.1704	1	6362.21		
621.1605	1	7068.67		
668.1617	1	28895.13		
669.1652	1	12566.74		
719.159	1	34695.09	C32 H30 O12	(M+CF3COO)-
720.163	1	15856.56	C32 H30 O12	(M+CF3COO)-

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C32 H30 O12	606.1737	719.1593	719.1590	0.0	-0.1	18.0000

Figure S16. HRESIMS spectrum of **2**

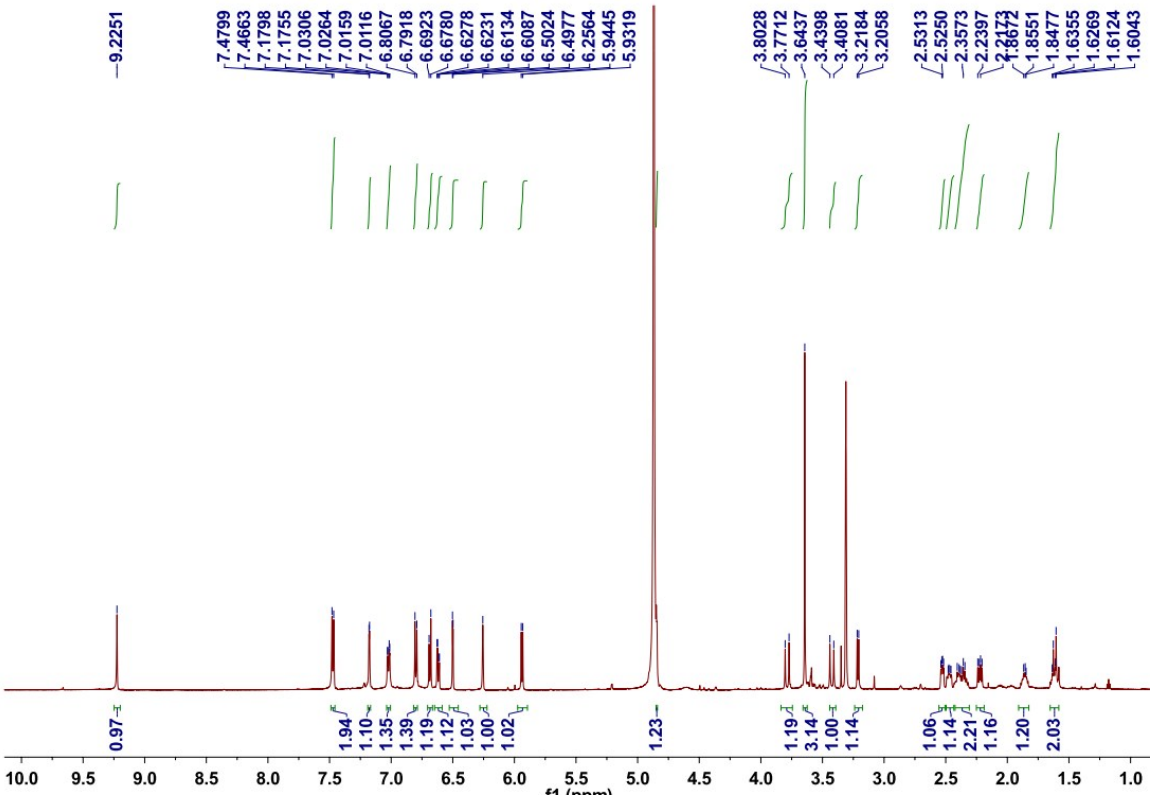


Figure S17. ^{1}H NMR spectrum of **3** in methanol-d_4

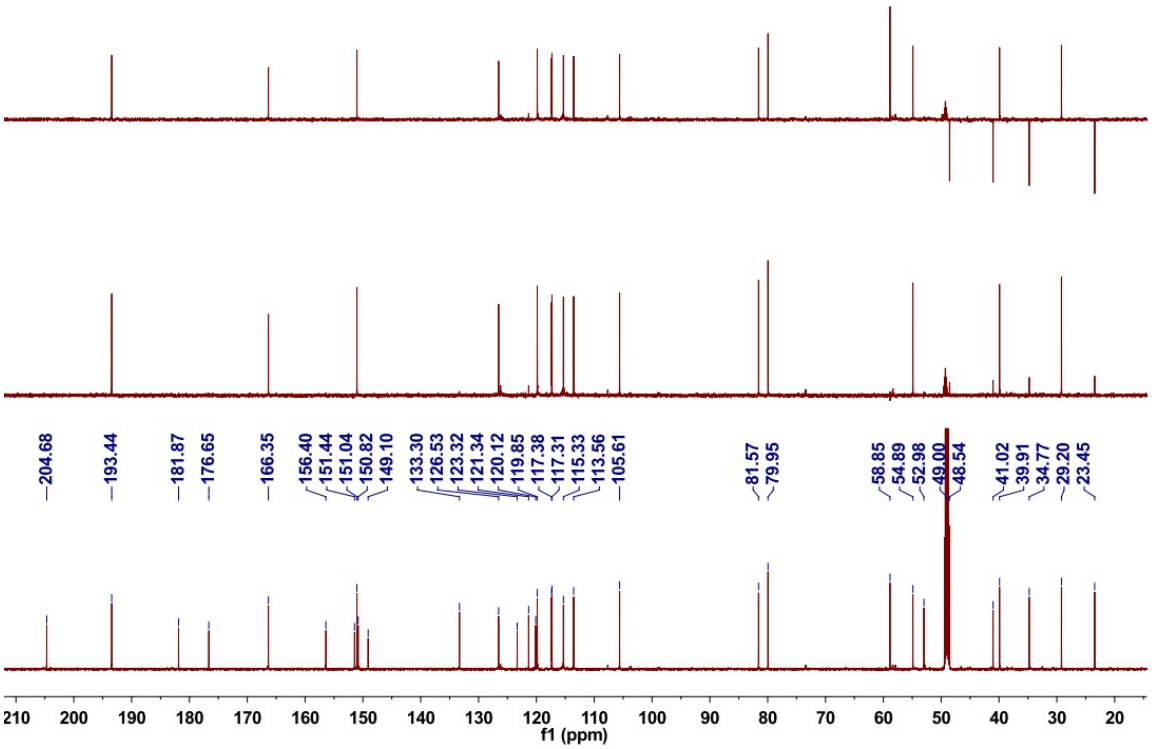


Figure S18. ^{13}C NMR and DEPT spectra of **3** in methanol-d_4

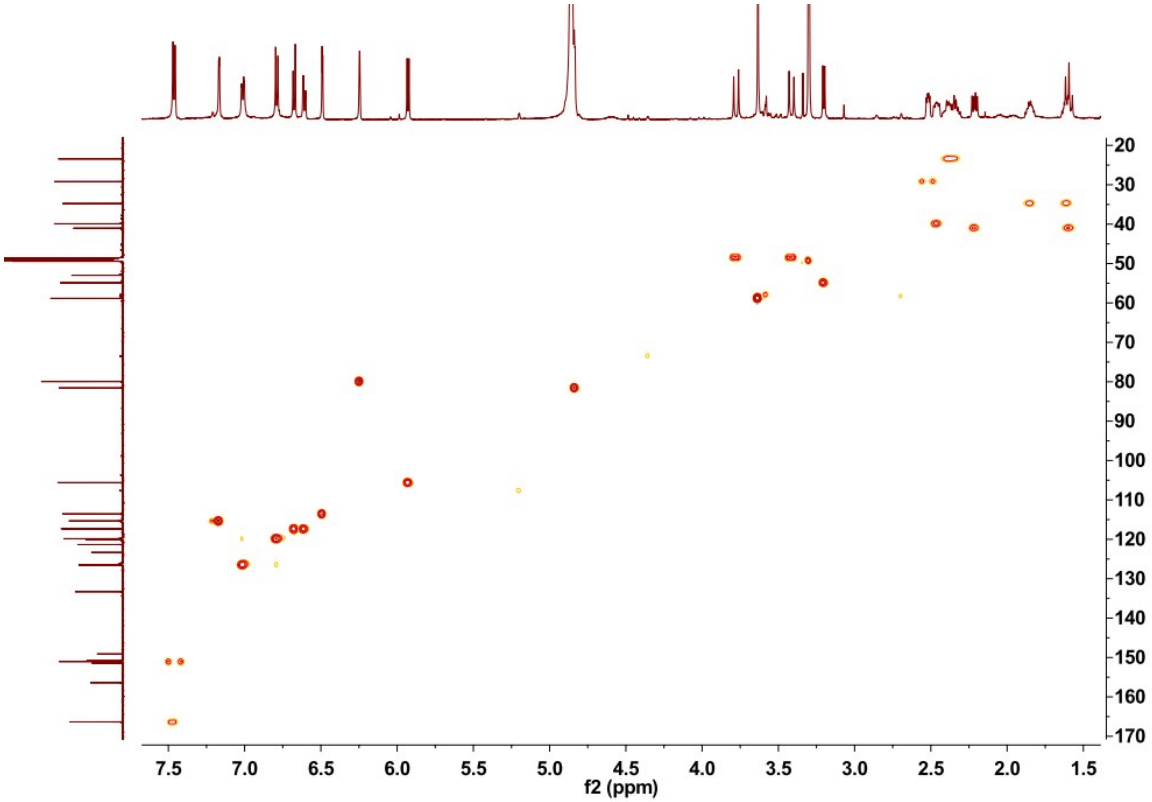


Figure S19. HSQC spectrum of **3** in methanol-d_4

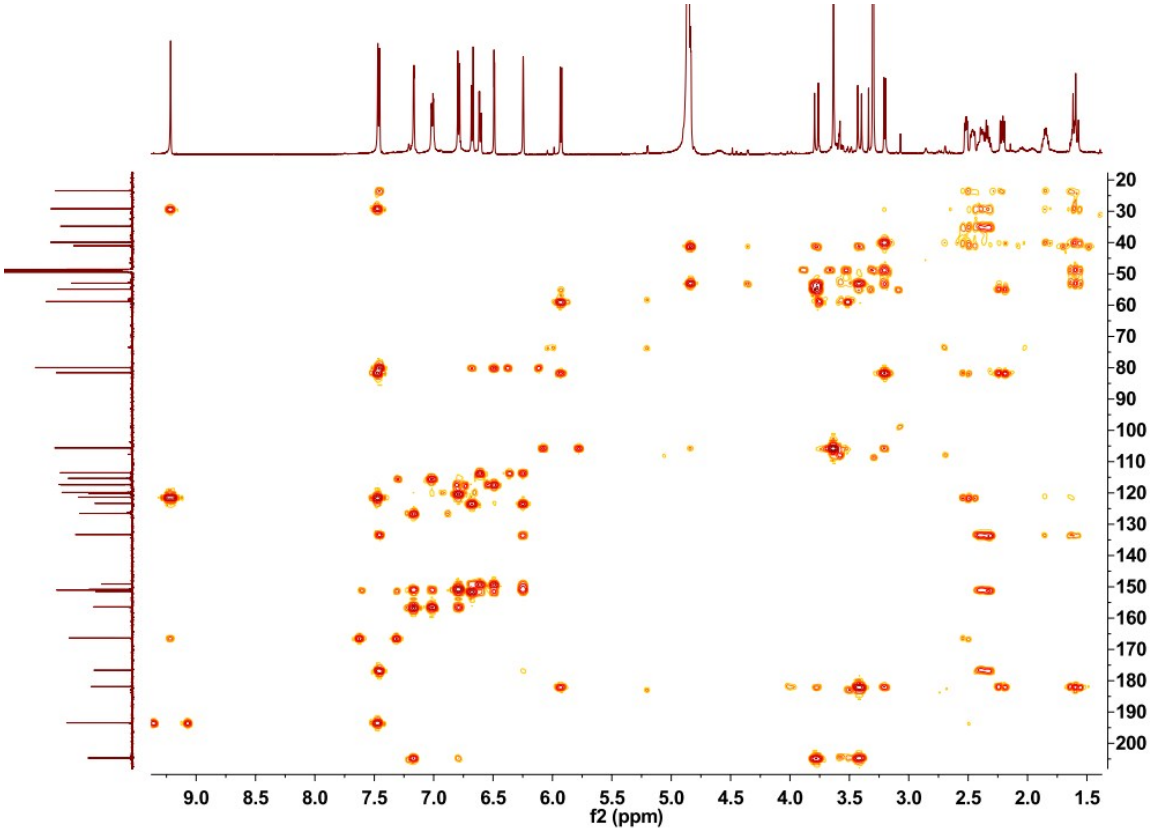


Figure S20. HMBC spectrum of **3** in methanol-d_4

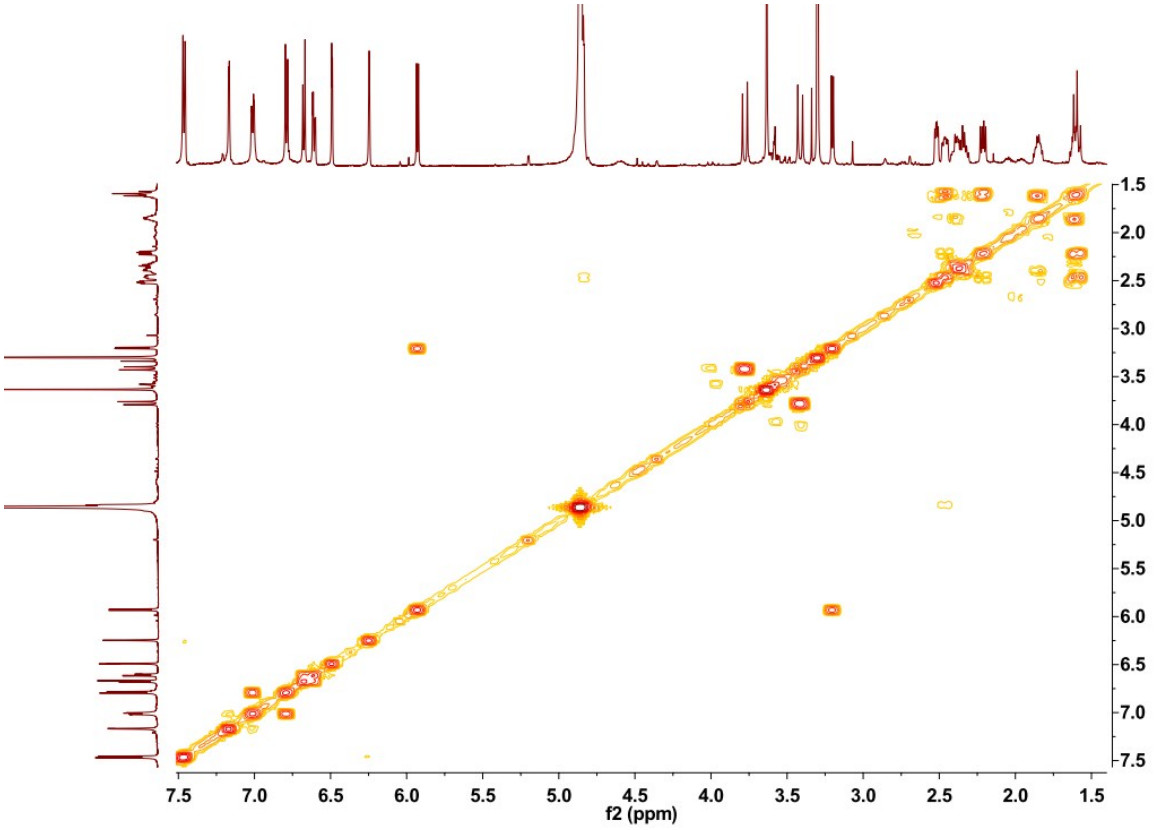


Figure S21. ^{1}H-^{1}H COSY spectrum of **3** in methanol-d_4

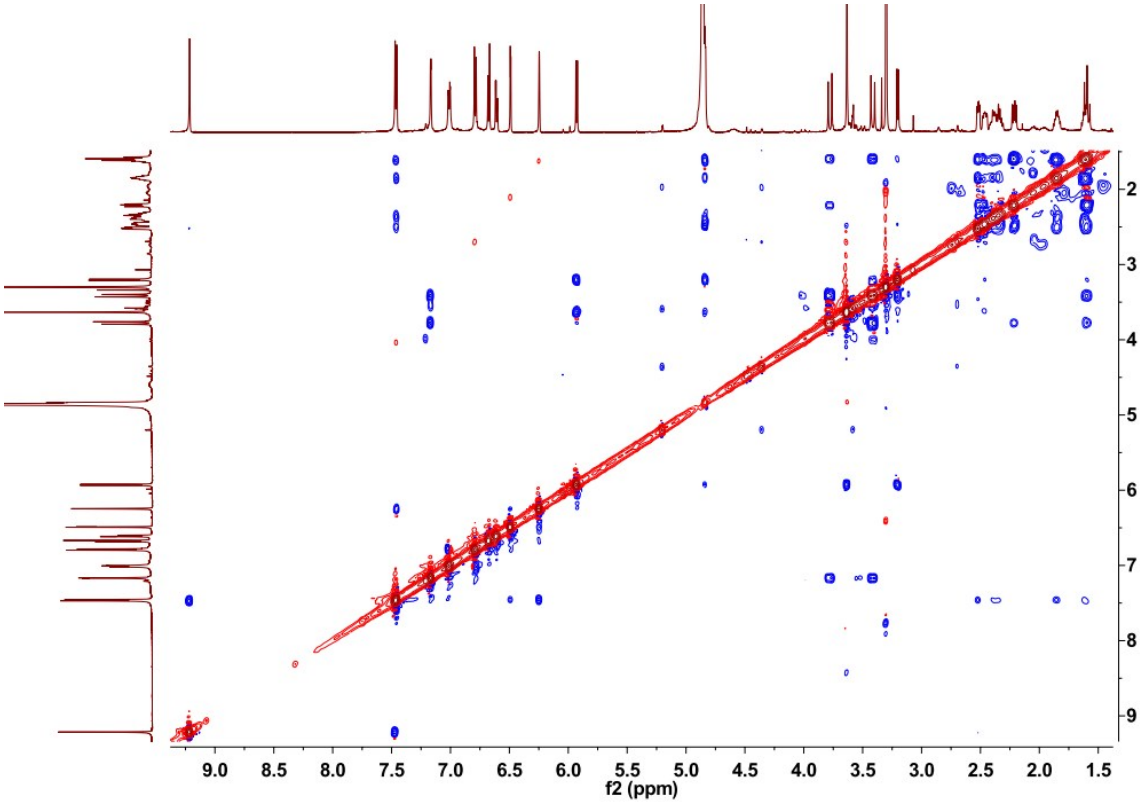
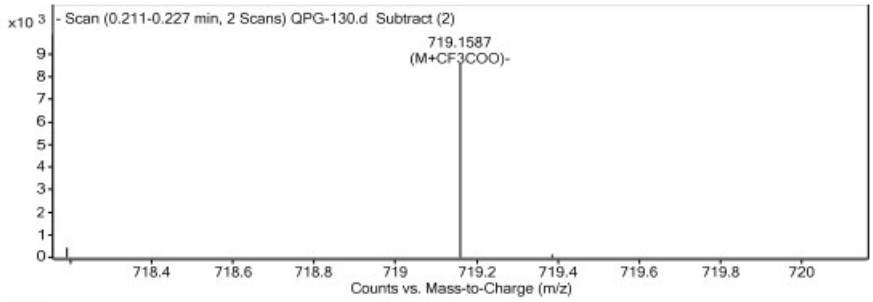


Figure S22. ROESY spectrum of **3** in methanol-d_4

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
605.1668	1	3996.36		
621.161	1	2290.44		
668.1623	1	7725.01		
669.1655	1	3127.76		
716.1814	1	2733.9		
719.1587	1	8532.68	C32 H30 O12	(M+CF3COO)-
720.1616	1	3958.71	C32 H30 O12	(M+CF3COO)-
767.18	1	3240.69		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C32 H30 O12	606.1737	719.1593	719.1587	0.9	1.4	18.0000

Figure S23. HRESIMS spectrum of **3**

3. The detailed isolation procedures

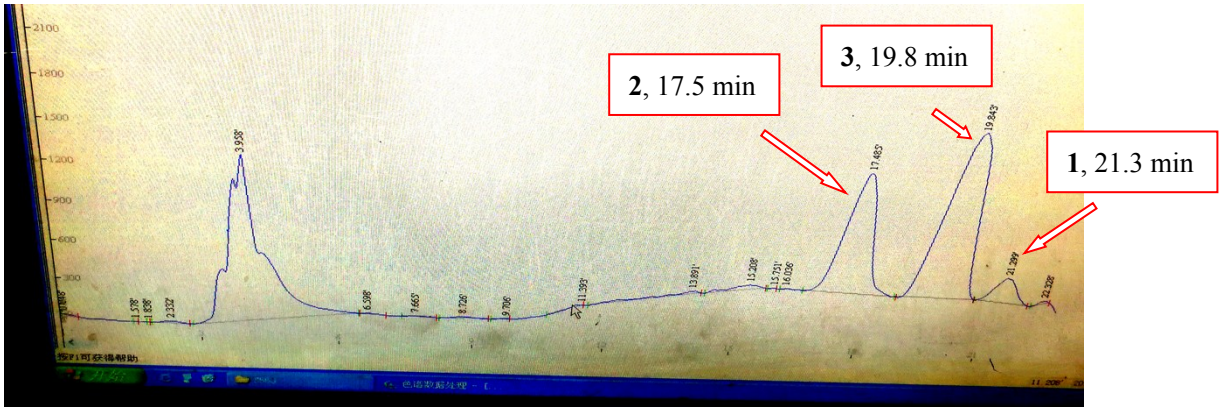


Figure S24. HPLC chromatogram of **1–3**, the chromatographic conditions: a LC-3000 high liquid chromatograph that made in China, a Zorbax SB-C_{18} column (250 × 9.4 mm, i.d., 5 μm), flow rate: 2.5.0 mL/min, detection at 210 nm, at 25 °C, mobile phase (MeOH–H_2O, 59:41).

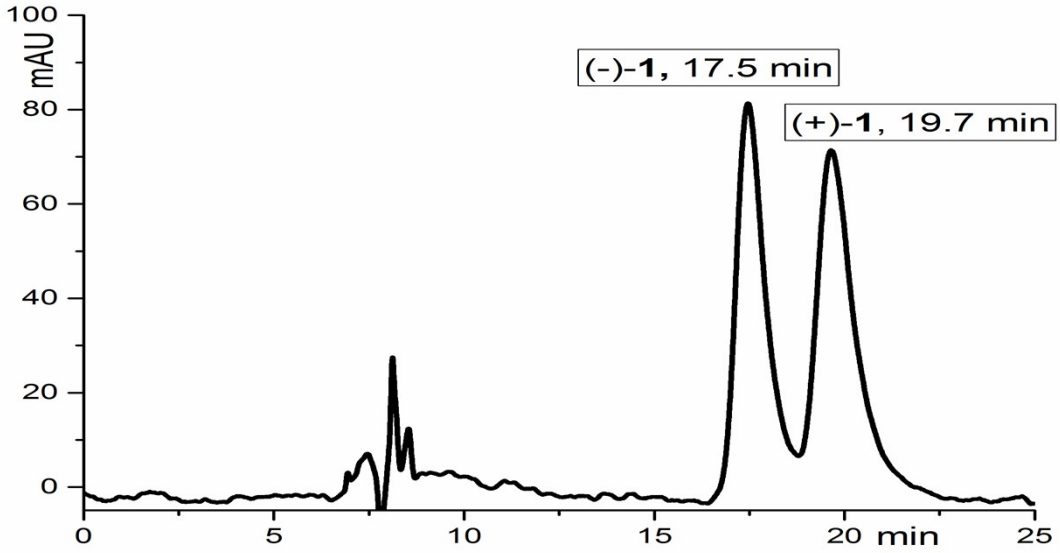


Figure S25. Chiral HPLC chromatogram of (–)-**1** and (+)-**1**, the chromatographic conditions: an Agilent 1200 liquid chromatograph, a 250 mm × 10 mm, i.d., 5 μm, Daicel Chiralpak (IC), flow rate: 2.5 mL/min, detection at 210 nm, at 25 °C, mobile phase (*n*-hexane–EtOH–HCOOH, 80:20:0.01%).

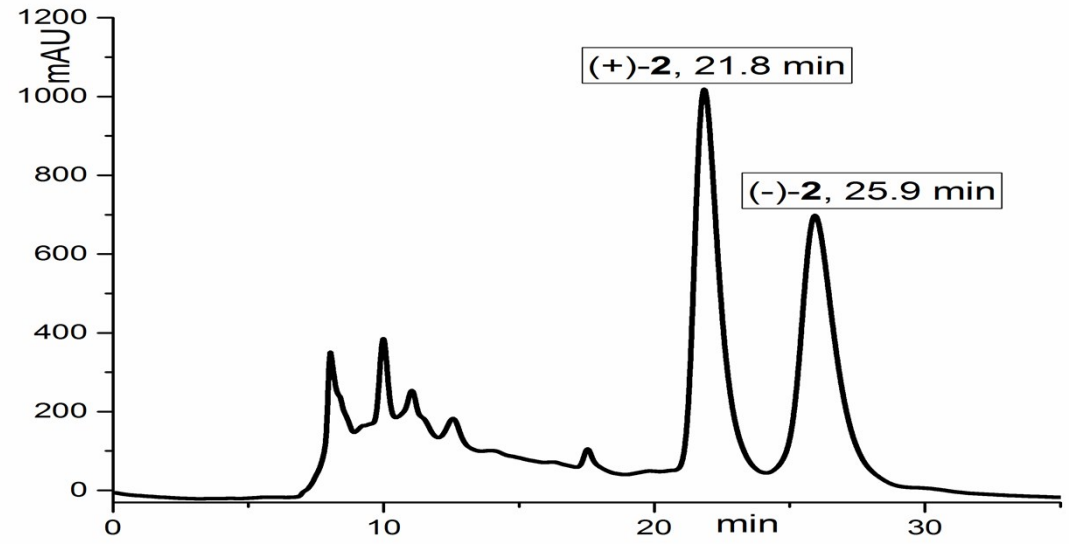


Figure S26. Chiral HPLC chromatogram of (+)-**2** and (–)-**2**, the chromatographic conditions: an Agilent 1200 liquid chromatograph, a 250 mm × 10 mm, i.d., 5 μm, Daicel Chiralpak (IC), flow rate: 2.5 mL/min, detection at 210 nm, at 25 °C, mobile phase (*n*-hexane–EtOH, 80:20).

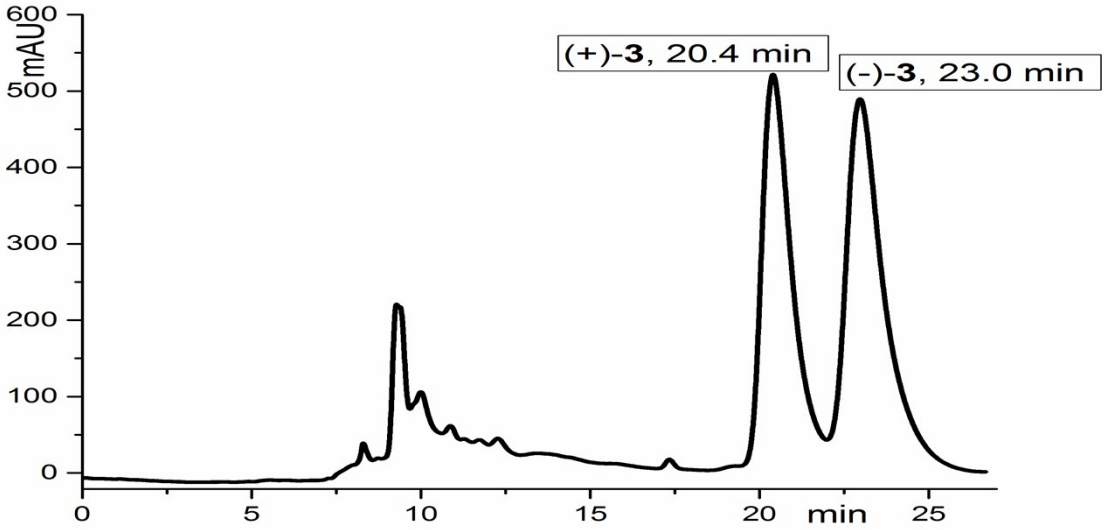


Figure S27. Chiral HPLC chromatogram of (+)-**3** and (–)-**3**, the chromatographic conditions: an Agilent 1200 liquid chromatograph, a 250 mm × 10 mm, i.d., 5 μm, Daicel Chiralpak (IC), flow rate: 2.5 mL/min, detection at 210 nm, at 25 °C, mobile phase (*n*-hexane–EtOH, 80:20).